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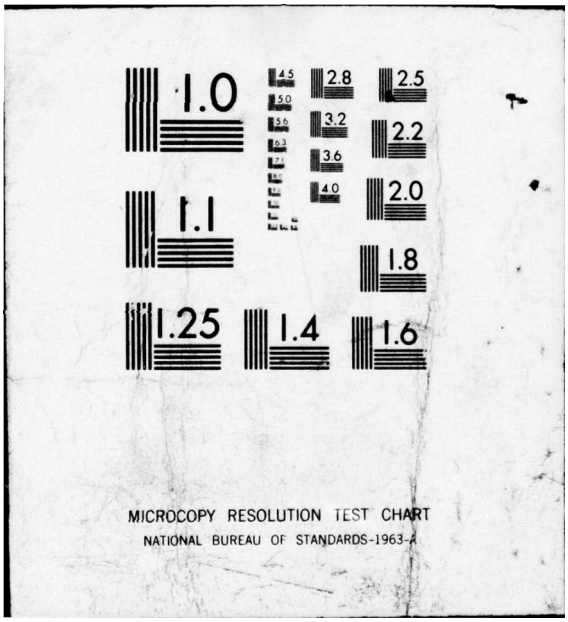
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OZONE OXIDATION OF METAL PLATING CYANIDE WASTEWATER

CPAC INCORPORATED
2364 LEICESTER ROAD
LEICESTER, NEW YORK 14481

SEPTEMBER 1976

FINAL REPORT: JUNE 1974 - SEPTEMBER 1975

AIR FORCE CIVIL ENGINEERING CENTER
(AIR FORCE SYSTEMS COMMAND)
TYNDALL AIR FORCE BASE
FLORIDA 32401

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Electroplating facilities, as associated with aircraft engine maintenance bases operated by the Air Force, generate quantities of wastewater contaminated with cyanides. Although traditionally treated with chlorine, a process was developed by the Houston Research Corporation under Contract No. F29601-72-C-0065 using ozone to oxidize the cyanides. A demonstration plant was designed by CPAC and installed at Tinker Air Force Base to treat 3000 gallons per month of primarily nickel
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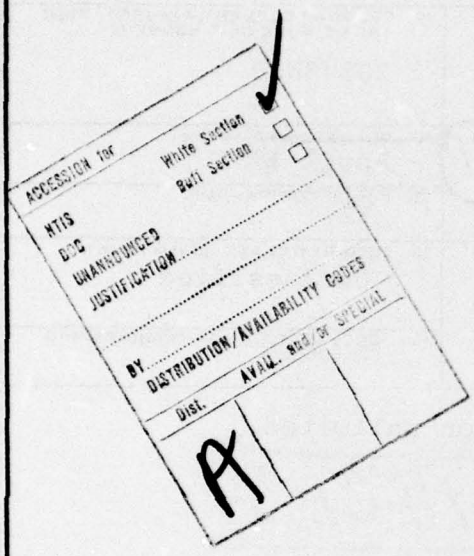
cont.

strip waste at concentrations up to 50,000 mg/l of total cyanide. A series of test runs proved ozone to be very effective and economically competitive for the destruction of simple cyanides and most metal complexes. The iron complex proved to be very difficult to destroy even in the presence of UV light and elevated (150°F) temperature.



PREFACE

This report was prepared by CPAC, Inc., Leicester NY, under contract FO8638-74-C-0014. The research was performed under Program Element 64708F, Project 2054.

Inclusive dates of the research were June 1974 through September 1975. The report was submitted April 1976 by the Air Force Civil Engineering project officer, Captain Brian D. Bennett.

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This technical report has been reviewed and is approved for publication.

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SECTION I

INTRODUCTION

The toxicity of cyanides and the need to properly treat wastewaters containing cyanide compounds is well-known and accepted by significant users of such chemicals. Two major industrial sources of wastewater containing cyanides are metal plating plants and (color) photographic processing laboratories.

The Air Force has several aircraft engine maintenance facilities where electroplating operations are carried out. Wastewaters from these operations are usually treated by the alkaline chlorination process (Reference 1). In this process, chlorine gas is bubbled into a batch tank of cyanide waste for several days. In addition to the usual problems associated with storing and handling large quantities of chemicals, the chlorination process does not adequately treat all of the metal-complexed cyanides, so an alternative process was sought.

A process was developed using ozone and ultraviolet light to oxidize various types of cyanide wastes to produce an effluent containing no detectable cyanides. This work was reported in AFWL-TR-73-212.

The process, as developed, uses ozone to oxidize both free and complex cyanides to cyanates in concentrated waste solutions.

$$O_3 + NaCN + M(CN)_x \xrightarrow{UV} NaCNO + M(CNO)_x + O_2$$

Not all complexed iron cyanides are oxidized by ozone alone. A final treatment step providing greater bond-breaking energy is necessary. This step uses ozone, elevated cyanide solution temperatures (130° to 150°F), and the presence of UV light emissions to destroy the remaining cyanide (Reference 2).

Based on the results of research, a plant was designed to treat 3000 gallons per month of primarily nickel strip wastes at total cyanide concentrations up to 50,000 mg/l, with continuous operation, 24 hours per day and 5 days per week. A goal of no detectable cyanides in the final effluent was established.

SECTION II

DESIGN

1. DESIGN BASIS

Design of the plant installed in Building No. 3514 at Tinker Air Force Base, Oklahoma, was based on information in Reference 2 and the following parameters:

a. Waste Flow Rate

3000 gallons per month running 24 hours, 20 days per month. This equates to 6.25 gallons per hour.

b. Waste Influent Quality

50,000 mg/l (0.42 lb/gal) of total cyanide.

c. Cyanide Input Rate

1187 g/hr or 62.8 lb/day.

d. Waste Effluent Quality

Lowest detectable limit for total cyanides as determined by the 13th Edition of Standard Methods for the Examination of Water and Wastewater.

e. Water Feed Rate (Max)

Four times the waste feed rate or 25 gph. (Primarily to replace evaporation losses.)

f. Ozone Feed Rate

(2.4 grams O_3 per gram CN) 2850 g/hr or 150 lb/day.

g. Ozone Generator Power Requirements

Allowing 21 watt-hours per gram of ozone, a power supply of 60,000 watts (60 kw) is required. Power consumption data for Lowther cells in the range of 6.3 to 8.8 kwh/lb (13.9 to 19.4 watt-hours/gram) have been reported (Reference 3) using air feed. Air

quality and heat removal are both critical to the power efficiency obtained. The contractor's experience in measuring O_3 output from many field installations indicates a more practical range to be 19 to 22 watt-hours/gram.

h. Total Power Requirements

Total power required at full design output is 160,000 watts (160 kw).

i. Cooling Water Rate

3 gpm for compressor aftercoolers.

j. Ventilation Requirements

Room air ventilation rate to remove heat from compressors and ozone generators is 15,000 cfm at ambient temperatures above 85°F.

2. SYSTEM DESIGN

Figures 1 and 2 are flow diagrams showing how the individual equipment components are integrated into a complete treatment system. For descriptive purposes, the plant may be considered as three separate functional systems: Air preparation, ozone generation, and cyanide treatment. The complete plant requires a minimum floor space of 20 x 40 feet or 800 sq ft to allow for practical operating and maintenance access.

a. Air Preparation System

Air used to feed the ozone generators must be clean and dry to maintain efficient use of power and protect the dielectric plates in the individual cells. This is achieved by compressing the air to approximately 100 psig, cooling the air to condense out some of the water, and drying it to a dewpoint of between -40°F and -50°F in a self-regenerative desiccant-type of dryer.

Three 25 hp compressors (K-1, K-2, K-3) are used; each with a capability of compressing 100 scfm of air to 100 psig. Oil is circulated between the compressing screws and an air-cooled radiator to remove heat. A

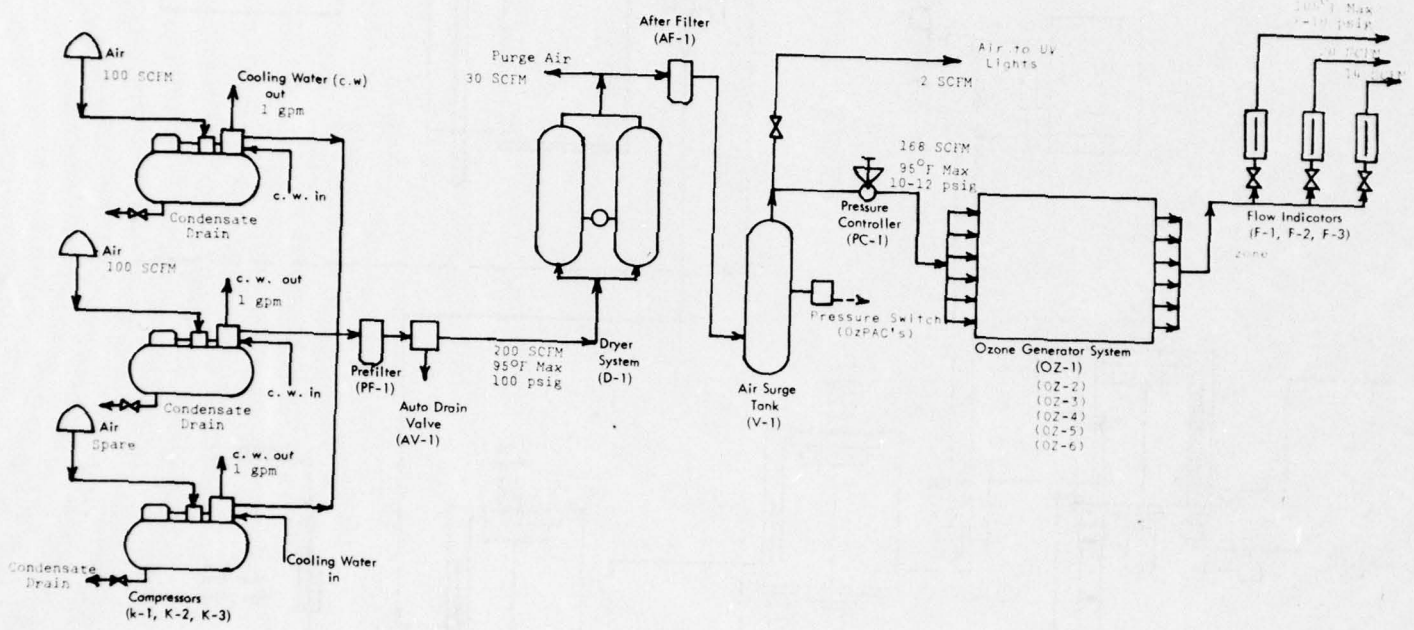

Figure 1. Flow Diagram - Ozone-Air System

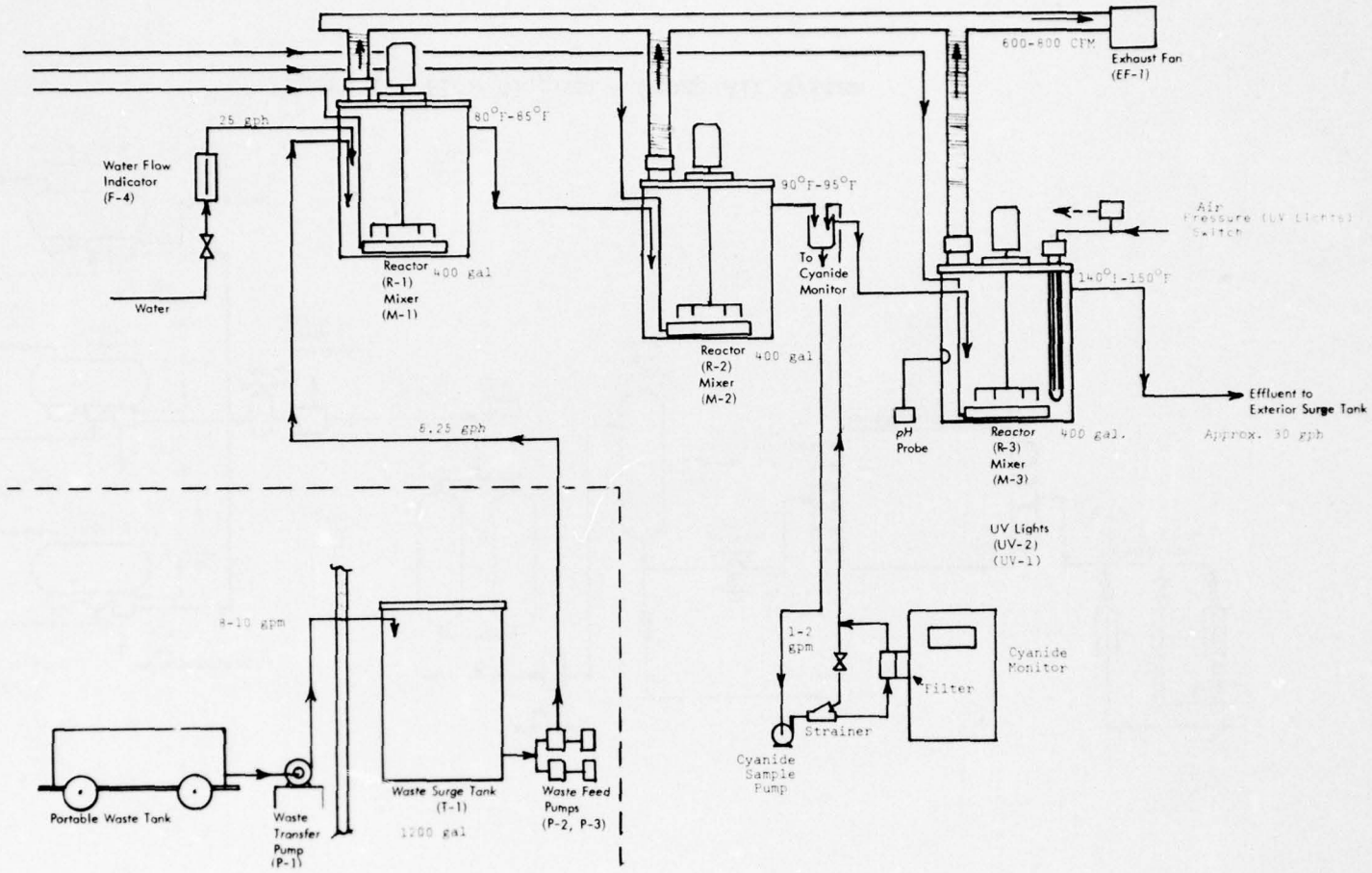

Figure 2. Flow Diagram - Cyanide Reaction System

water-cooled aftercooler reduces temperature of the compressed air causing most of the moisture to condense. The condensate and air then separate in the air surge tank located below each compressor. The condensate is periodically drained to the sewer through manual valves. Each compressor has automatic pressure and temperature controls and may be operated in either one of two modes of control. The "Auto" switch will allow the pressure controller to start and stop the drive motor, as required, to maintain desired pressure in the surge tank. The "Const" switch will also automatically maintain the desired pressure but does so by unloading the air intake valves while the drive motor remains ON.

From the compressor surge tanks, air flows through a prefilter to the dryer. The prefilter (PF-1) is a cartridge type filter used to entrain any droplets of oil or water that might be carried out of the air compressor surge tanks and thus protects against oil-fouling of the desiccant charge in the dryer.

The dryer (D-1) has twin desiccant chambers (Figure 3), one of which is "on-line" while the other is being regenerated. Regeneration and switching of operating valves occurs every 5 minutes and is automatically controlled by an electrical timer and solenoids. Desiccant is regenerated by purging a slipstream of dry air from the on-line chamber through the "wet" chamber at reduced pressure. At full line pressure of 100 psig, the air is dried to a -40°F dewpoint or better.

From the dryer, air flows through a cartridge-type after-filter (AF-1) where any desiccant dust is removed, and on into a surge tank (V-1). The only function of the surge tank is to smooth out pressure-flow fluctuations that might occur from dryer chamber switchings.

From the surge tank, air is piped to a pressure control valve (PC-1) where the pressure is reduced to the desired (10 to 12 psig) operating level for use in the ozone generator system.

b. Ozone Generation System

The ozone generation system includes six separately controlled sets of generator cells (OZ-1, OZ-2, OZ-3, OZ-4, OZ-5, OZ-6), 30 cells to a set. There are three console

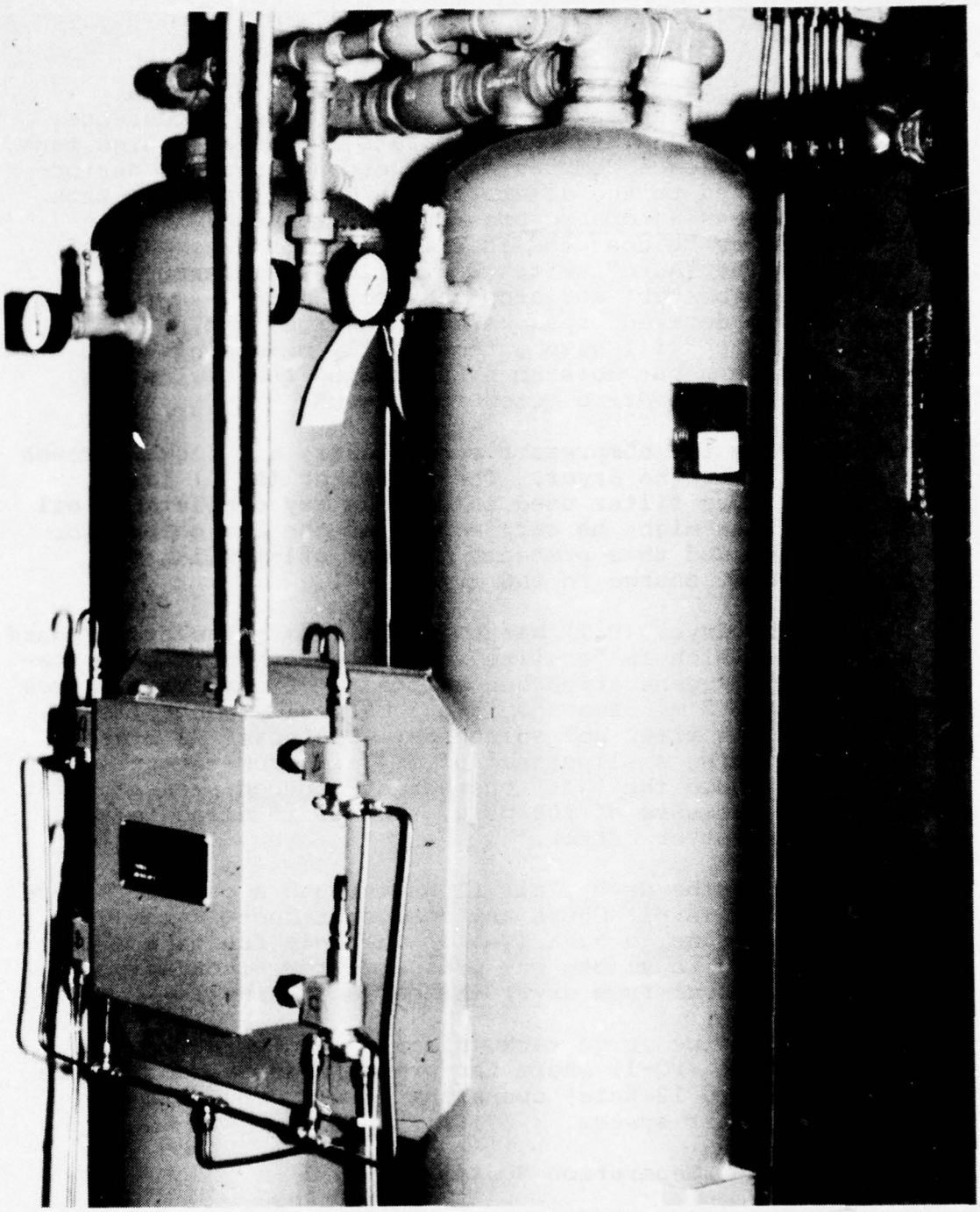

Figure 3. Air Dryer

cabinets (Figure 4) with each containing two sets of cells and all associated power control and cooling equipment. Each set of 30 cells has a nominal output capacity of 1 pound per hour of ozone at a concentration of approximately 1/2 to 1 percent in the airstream passing through the generator.

Each console has a control panel with dual sets of controls so that each of the six cell sets may be operated individually. The center console also has a master panel for simultaneous control of all six sets.

Ozone generator cells are located in the bottom front section of each console with the cooling fan in the rear. Air is pulled in through ventilation screens on the front of each unit and is exhausted at the rear. Power transformers and solid state control components are mounted on racks in the upper section of each console.

Since the natural rate of decomposition of ozone increases with increasing temperature (Reference 4), it is important that the supply of cooling air to the generator cells not be restricted or impeded in any way.

Air inlet and air-ozone outlet manifolds are mounted above the consoles at the rear where individual piping runs lead into each of the three console cabinets. Ozone output from all six generators is manifolded into a common line and piped to the rotameters at each of the three reactors.

The console cabinets have a supporting framework of 3/4-inch square tubular stainless steel covered with ABS plastic panels. The top, side, and rear panels may be removed for access to the inner components of the system.

Controls and operating instruments for each of the six generators include: (See Figure 5.)

-Pressure gage on air feed line.

-Flow indicator (rotameter) and manual valve to adjust the flow.

-Ammeter and voltmeter.

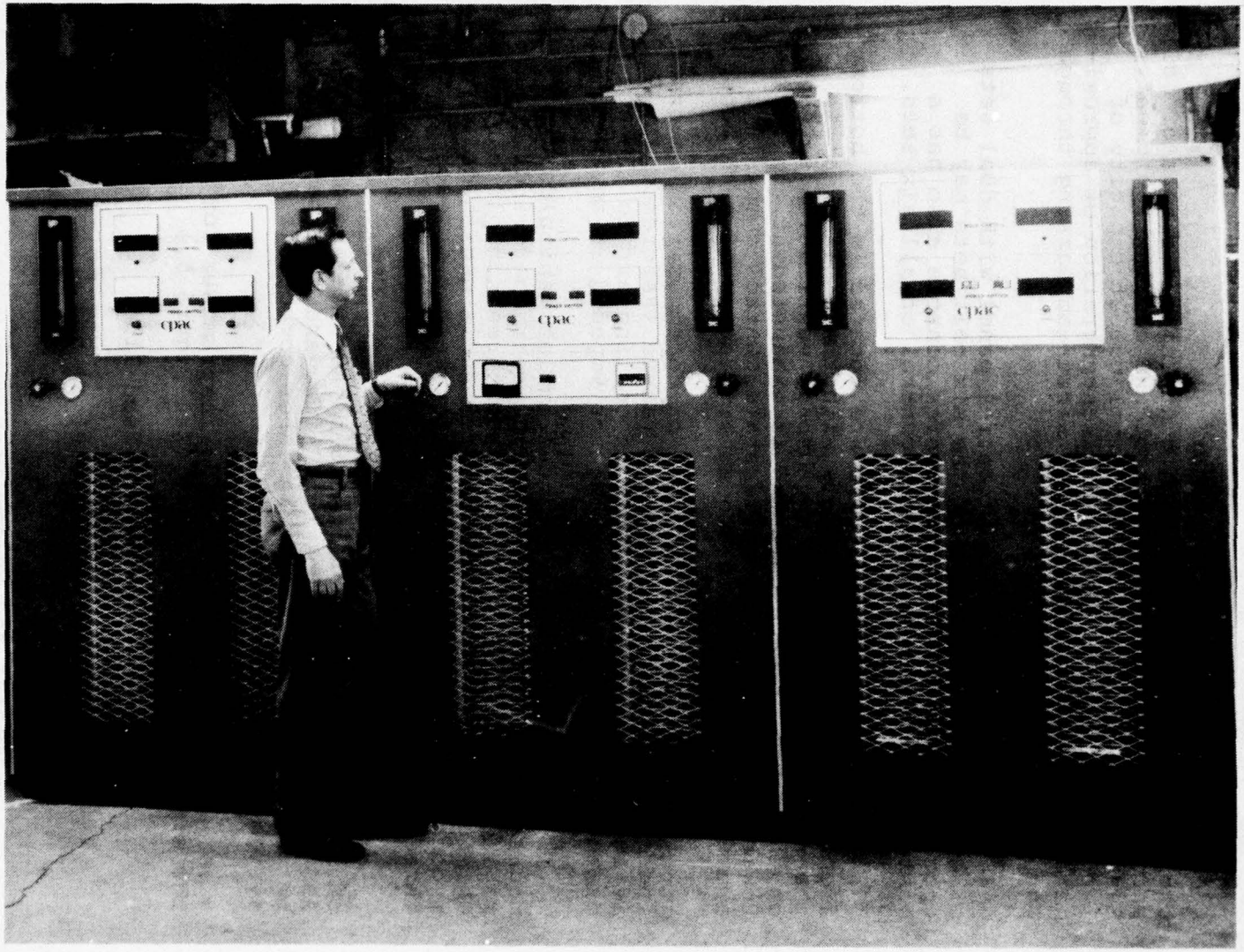

Figure 4. Ozone Generator

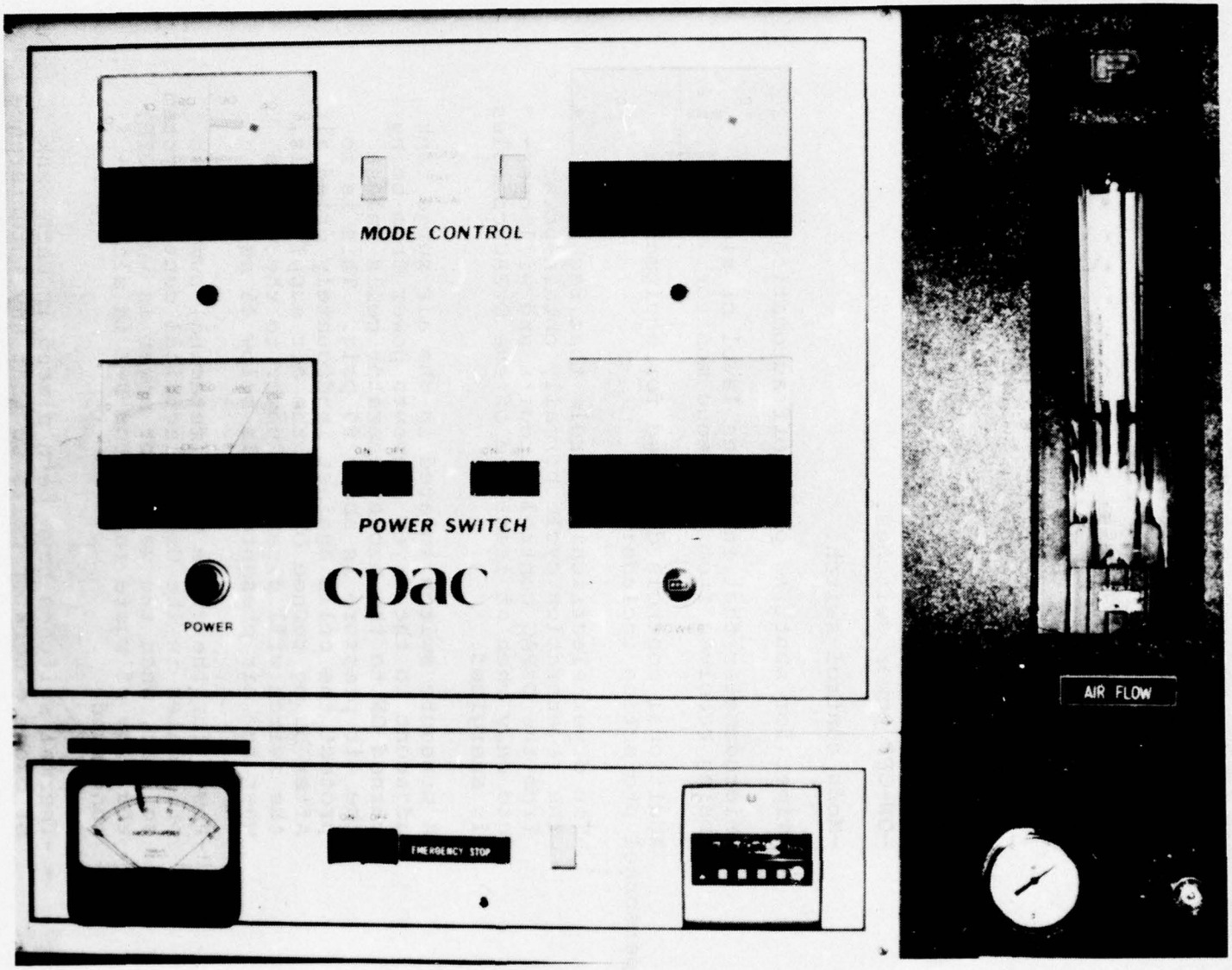

Figure 5. Ozone Generator Control Panel

-Power control knob.

-ON-OFF power switches.

-Running light.

-Auto-Manual mode control switch.

The master control panel on the center console includes:

-ON-OFF power switches.

-Mode control switch.

-Timer for shutting power off automatically.

-Microammeter that indicates level of signal being received from the ozone monitor.

Additional controls designed for equipment or personnel protection include:

-The dryer electrical controls that regulate the regeneration cycle normally obtain power from the OzPAC control circuits and will operate only when at least one of the OzPAC consoles is energized.

-A pressure switch located in the air surge tank adjacent to the dryer prevents power from being turned ON to the ozone generator cells unless the air pressure is above 80 psig. This is to protect the cells against inadequately dried air. After being turned ON, if the air supply fails, the switch will disengage power to the OzPACs when the air pressure falls below 45 psig.

-Power for the waste feed (metering) pumps also originates in the OzPAC electrical control system so that, when the generator power is turned OFF, the flow of waste to reactor R-1 is also discontinued.

-Thermal switches have been placed in each bank of ozone generator cells so that any interference

with the flow of cooling air, causing a rise in temperature above 200°F, will result in power being shut off to the ozone cells.

-Each pair (15 pairs per 30 cell set) of ozone generator cells is fused with a 250 volt, 1/2 amp fuse to protect against power surge damage. These are accessible only through the front panel of the OzPACs.

-Each of the six ozone generator units has a motor starter with circuit breaker inside the rear panel. This breaker may be reset without removing the panel by use of a convenience hole in the panel.

-Each of the six ozone generator units has a special KAB-70 (250 volt, 70 amp) fuse located in the power supply section in the rear of the OzPAC console. The rear panel must be removed to change this fuse.

c. Cyanide Treatment System

Cyanide waste is delivered in portable (wheel-mounted tanks) (Figure 6) to a transfer pumping station (Figure 7) at the southwest corner of Building 3514. A flexible hose is used to connect the tank to a transfer pump (P-1) which transfers the waste to a fiberglass storage tank (T-1) located inside the building.

Located adjacent to the waste storage tank are two metering pumps (P-2, P-3) used to feed cyanide waste to the R-1 Reactor. These pumps have adjustable outputs and each is set to pump at a rate of 6-1/4 gallons per hour. Only one pump is operated at any one time; the second pump being available as a spare. Neither pump is operable unless power is ON in the ozone generators.

Ozone must be brought into intimate contact with the liquid cyanide to efficiently and effectively complete the desired reaction. This is accomplished by using three reactors (R-1, R-2, R-3) in series through which the liquid flows by gravity, while the ozone-air mixture is parallel fed to each reactor. All reactors operate at atmospheric pressure and no provision is made for recycling offgases.

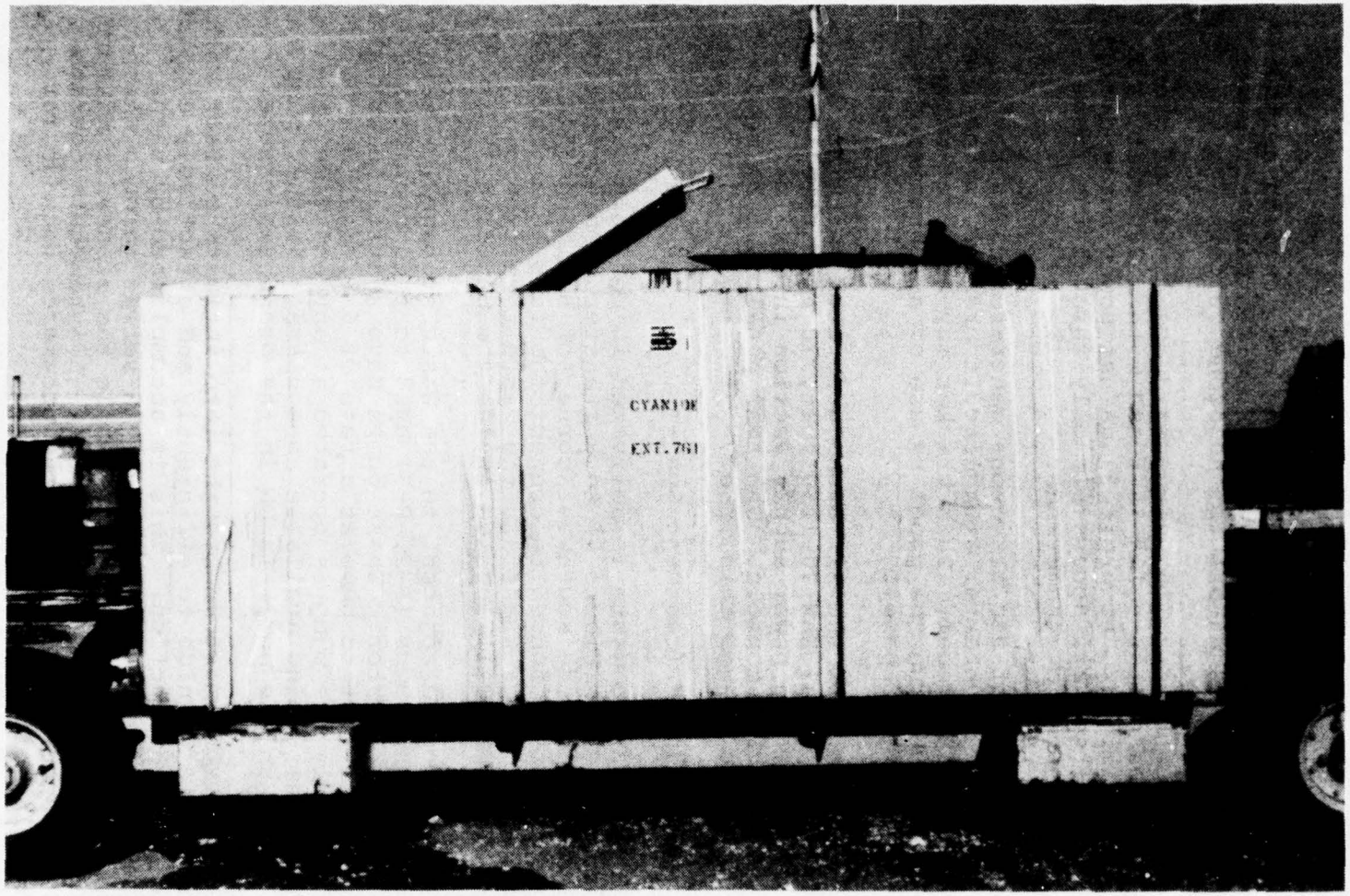

Figure 6. Portable Waste Tank

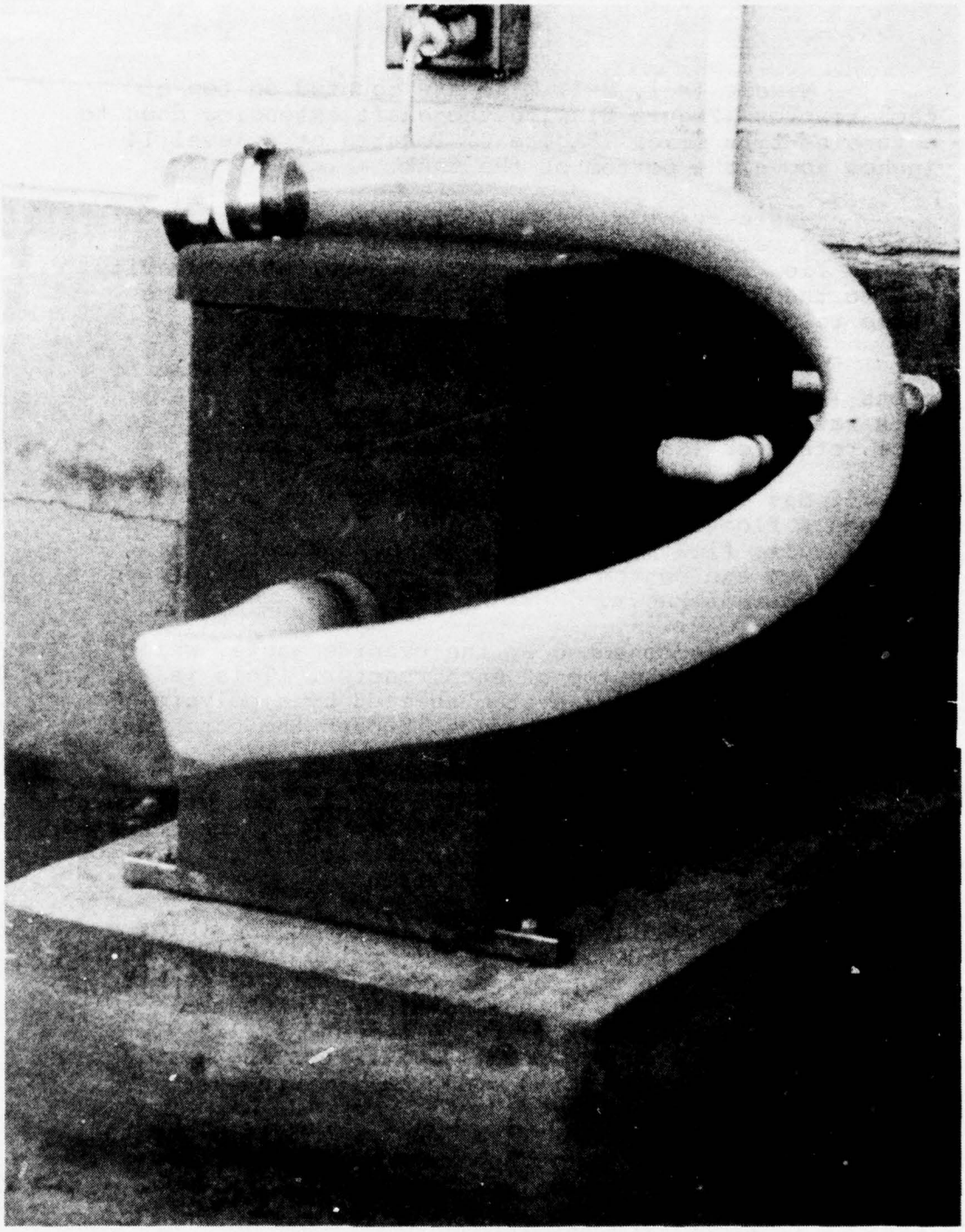

Figure 7. Waste Pumping Station

Mixers (M-1, M-2, M-3) are mounted on top of each reactor (Figure 8) with the shaft extending down to a turbine-type mixer (Figure 9) located at a level 14 inches above the bottom of the tank.

Waste cyanide is fed only to Reactor R-1 from where it overflows to Reactor R-2 and finally to R-3. Liquid flow through the system is controlled by gravity due to the different lengths of mounting legs on the three reactors.

Water is also fed to Reactor R-1 in a ratio of 4 parts (by volume) water to 1 part of waste cyanide. This rate is controlled by a manual valve and a float type rotameter (F-4) mounted next to the reactor.

Gas (air plus ozone) is fed to each reactor through a float-type rotameter (F-1, F-2, F-3) with manual valve flow rate adjustment. Gas enters the liquid near the bottom of the reactor by being forced through sparger tubes.

Ozone is consumed by the cyanide waste, while air escapes from the top of each reactor. This is collected in a PVC vent system powered by a polypropylene fan (EF-1) which exhausts through the north wall of the building.

Overflow liquid from No. 2 Reactor passes through a catch-basin, from which a portion of it is recirculated by a small sampling pump to an automatic cyanide monitor for analysis of cyanide concentration.

Reactor R-3 is equipped with two ultraviolet (UV) lights (UV-1, UV-2) placed in vertical Corex® glass wells. Cooling air is provided for the lights from a control box located on a shelf behind the reactor. A pressure switch is located in the air supply line to shut off power to the UV lights if the cooling air supply is interrupted for any reason (Figure 10).

Overflow effluent from Reactor R-3 is piped to outside in-ground tanks for storage until ready for disposal through the Base Industrial Waste Treatment Facilities. A sample tap is provided on the overflow line as it leaves the reactor.

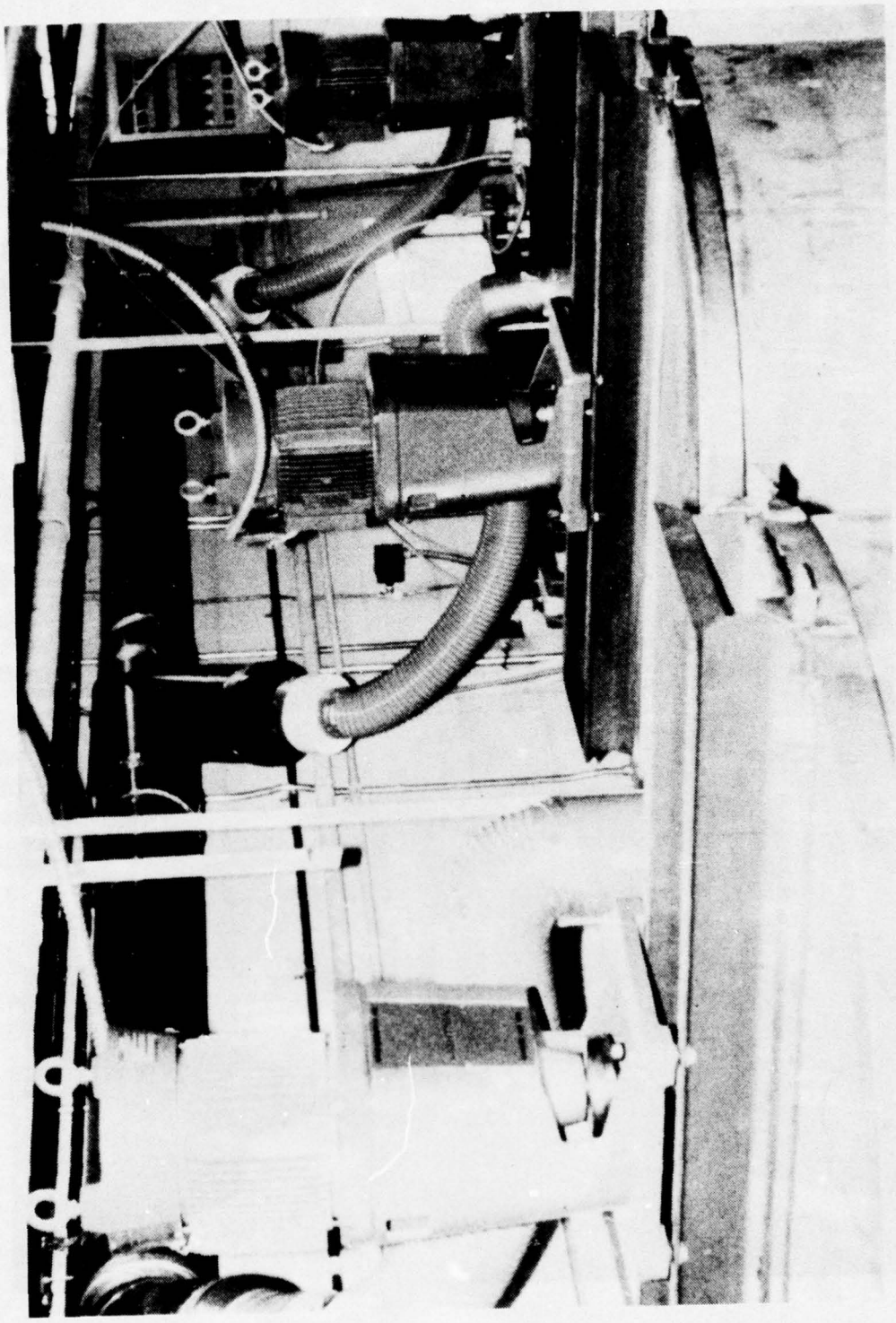

Figure 8. Reactor Vent System and Mixers

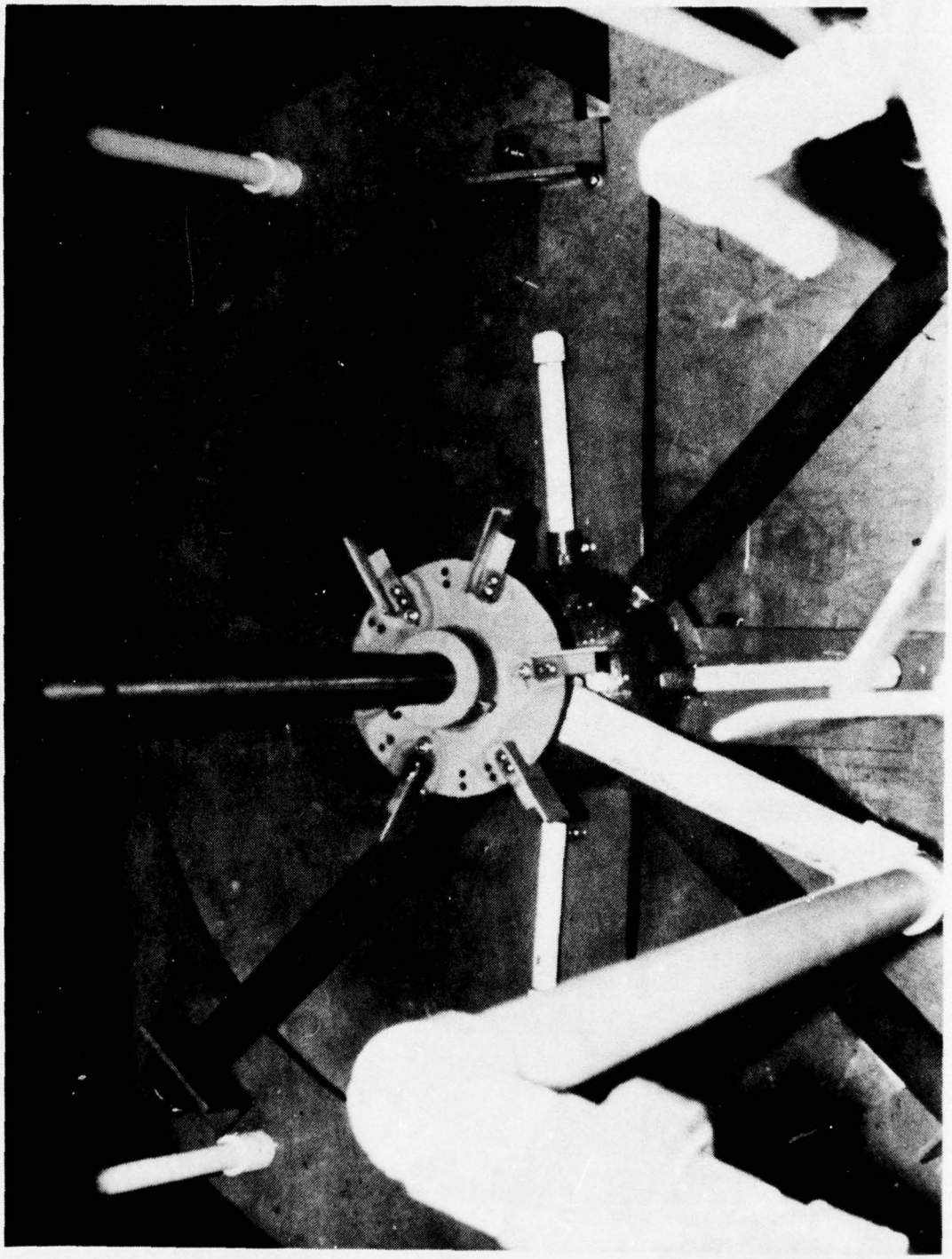

Figure 9. Reactor R-1 Sparger Assembly

An indicating pH meter is mounted on the shelf behind Reactor R-3 to continuously monitor the pH level of that reactor.

An ozone detector is also located on the same shelf to monitor air in the room for leaks and automatically shut off power to the ozone generators if a concentration of ozone above 1 ppm is detected (Figure 10).

3. EQUIPMENT DESIGN AND SELECTION

(Refer to Figures 1 and 2)

a. Waste Transfer Pump P-1

March Model AC5CMD, centrifugal 8 to 10 gpm at 10 to 15 feet head. This pump was selected to handle incoming concentrated waste because of its simplicity, nonmetallic construction and sealless magnetic drive.

b. Waste Surge Tank (T-1)

Raven Model C8E14 Fiberglass with B507C Cover, 1350 gallons, 5 feet diameter by 10 feet high. Cyanide waste is transported from the Plating Shop to the treatment area in 600-gallon portable trailer tanks. The surge tank was selected with a capacity to hold two trailer loads of liquid and still occupy only a minimum of operating area.

c. Waste Feed Metering Pumps (P-2, P-3)

Gorman-Rupp Model M-13325-3, adjustable pumping rate from 1 to 10 gallons per hour, positive displacement (bellows), plastic. These pumps were selected for simplicity, accurate pumping rate, and inertness to corrosive properties of waste. Only one pump is required for normal operation; the second pump is a spare.

d. Reaction Tanks (R-1, R-2, R-3)

United Utensils Model VT-500, 14 gallon type 304 stainless steel, 52-inch diameter, 58-inch straight side, total volume 500 gallons, working volume 400 gallons, well bottom, hinged (1/3) cover, four legs, adjustable for leveling. Tanks were selected for availability, corrosion resistance, ease of modification (as opposed to glass lined), and conformation.

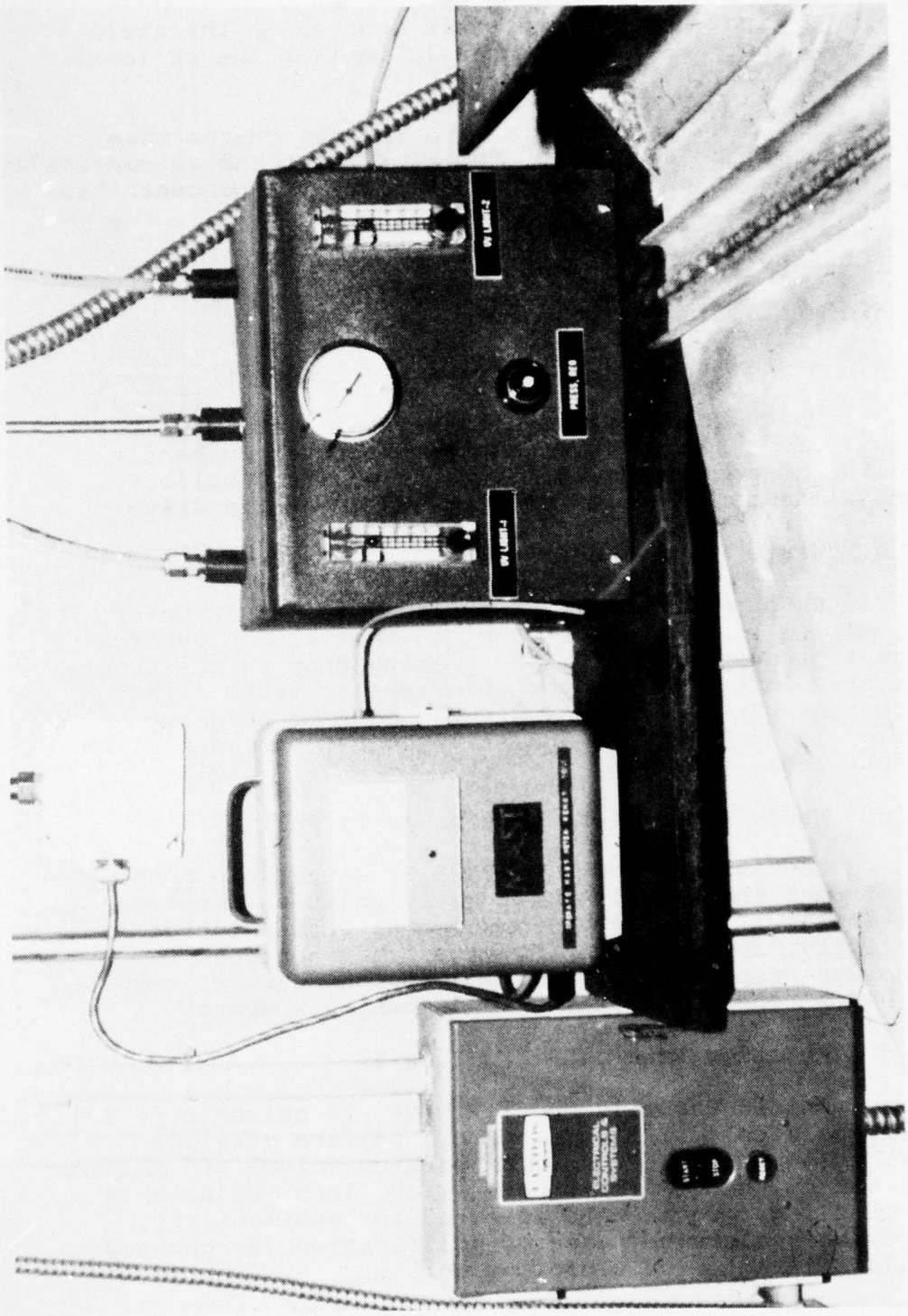

Figure 10. Ozone Monitor and UV Light Air Supply Controls

The reaction tanks are mounted in a line. All process liquid feed is to R-1 with gravity overflow from R-1 to R-2 to R-3 caused by an 8-inch differential in height between each reactor. The height differential was created by using different lengths of mounting legs on each reactor.

e. Reaction Mixers (M-1, M-2, M-3)

Lightning Model NLGD-300, 3 hp, top mounted, 48-inch long 316 SS shaft, SS mixer (turbine type) 11-inch diameter with 6 blades and a stabilizer ring.

The mixers were selected on the basis of a medium power-to-liquid volume ratio (7.5 hp per 1000 gallons) to maximize liquid-gas contacting time, availability, corrosion resistance, and ease of mounting. The mixer turbine is suspended approximately 14 inches above the bottom of each reactor to allow space below for gas spargers.

Two 14-inch channels (on sides) across the top of each reactor are used for mounting each vertical mixer.

f. Sparger Assemblies

CPAC No. 700040 cylindrical diffuser tubes, 1-3/4-inch OD by 1-inch ID by 18-inch length, closed one end, 1/2-inch PVC nipple other end, FAO-50-4, approximately 100-micron pore size. These ceramic tubes were selected for their contacting efficiency and excellent service life in numerous contractor installations.

All reactors are fitted with a wheel-type gas sparger assembly using the diffuser tubes as spokes mounted in a horizontal plane from a central PVC pipe cap hub. The cap is cemented to the center of a flat 1/4-inch PVC supporting wheel which also supports hold-down rings for the diffuser tubes. Gas is piped to the hub from which it flows outward through the diffusers. The entire assembly is held in place in the bottom of each reactor by a PVC pipe rack that extends up to and rests against the top of the reactor (Figure 9).

Reactor R-1 has eight diffuser tubes in its sparger assembly while R-2 and R-3 have four each.

g. Reactor Vent System

Agile Blower, with 8-inch connections, 1/3 hp, 800 cfm, fiberglass housing, polypropylene wheel, round PVC duct (Figure 8).

The all-plastic vent system was selected for durability and corrosion resistance. The fan has a capacity to exhaust three times the volume of air fed to the reaction system so that gas fumes will not escape into the operating area, when a reactor cover is lifted.

Vent connections to the reactors are 6-inch on R-1 and 4-inch on R-2 and R-3. Sections of flexible spiral hose connect each reactor to the main vent duct. A Koch 4-inch thick polypropylene flexi-mesh entrainment separator is located in each vent line where it attaches to the reactor cover.

h. Ultraviolet Lights (UV-1, UV-2)

Conrad Hanovia Model 19416.101 lamp well, silica glass, 3-1/2-inch OD, 50-inch length, Model 34980.101 stabilized control ballast, Model 077A0160 mercury vapor lamp, 42-inch length, 4500 watts.

Two lamp assemblies are installed vertically in Reactor R-3 approximately 4 inches from the tank wall and approximately 120 degrees apart. Each lamp emits the level of power indicated to be necessary by the HRC design.

Power wiring and cooling air lines enter the top of the light wells that project above the reactor cover (see Figure 11).

i. Air Compressors (K-1, K-2, K-3)

Joy Twistair® Model TA-025T2-5W, tank mounted, 100 scfm each, 100 psig discharge, oil circulation through compression screws to air cooler, water cooled aftercooler, dual automatic controls (Figure 12).

Air requirements for the ozone generators at design output of 150 lbs/day were calculated to be 130 scfm for a 1 percent concentration of ozone and 260 scfm for a concentration of 1/2 percent. A wide range of operating flexibility is achieved by using three compressors with a total capacity of 300 scfm. Although reserving 15 percent

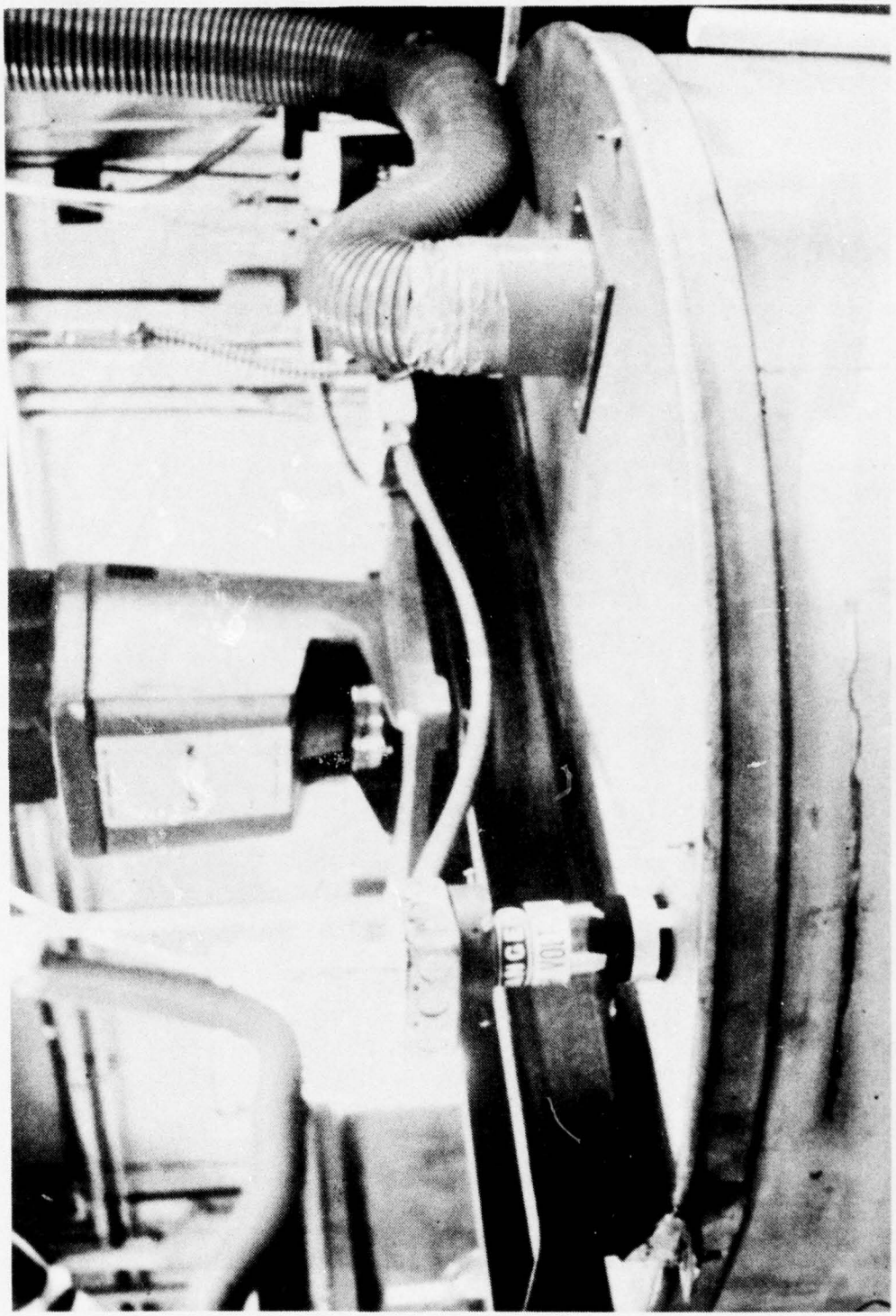

Figure 11. UV Lights

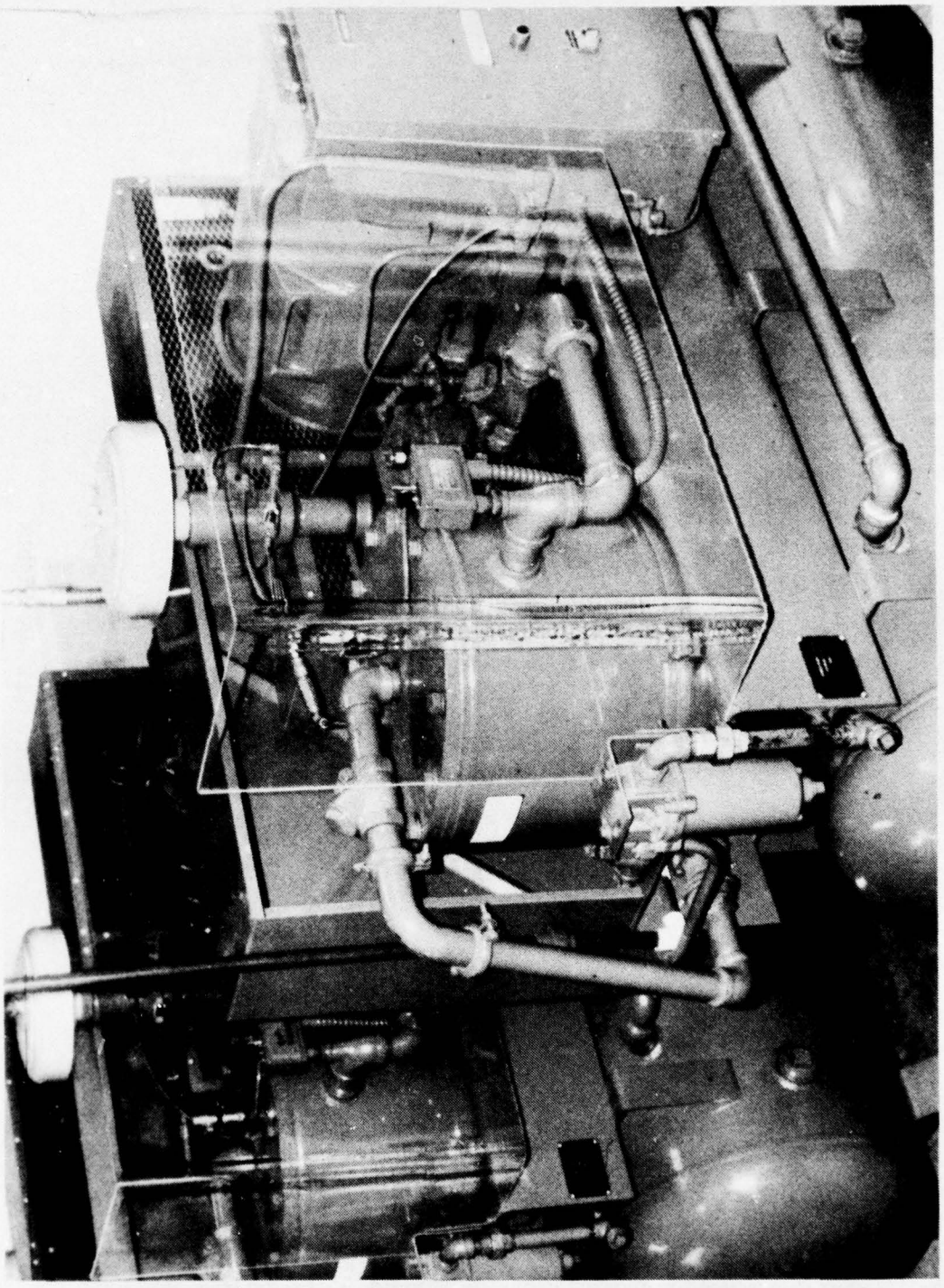

Figure 12. Air Compressors

of the capacity for the air dryer surge system, there is still sufficient compressor capacity to operate the generators at maximum ozone output well below a 1 percent concentration in air.

At design operating conditions, only two compressors are on line and the third is available as a spare.

When in operation, each compressor emits 75,000 Btu/hr of heat that must be removed through the air-cooled radiator. It is imperative, therefore, to have sufficient cooling air available in the operating area. This is provided for by using two exhaust fans mounted in the wall directly above the compressors.

j. Air Dryer Prefilter (PF-1)

Pall Trinity Model MEC100-9SU320, 6-1/2-inch OD by 40-inch length, 2-inch NPT connections, 9 cartridges (3 lines of 3 each). This filter was provided to protect the dryer by removing oil and/or moisture carried over from the compressor tanks. An automatic dump drain valve is mounted on the bottom of the filter to drain any liquid collected.

k. Air Dryer (D-1)

Pall Trinity Model 201HA1, heatless, self-regenerating, activated alumina desiccant, 100 psig operating pressure, -40°F dewpoint, automatic regeneration.

The dryer was selected to provide clean dry air for the ozone generators with a maximum dewpoint of -40°F at an air flow rate of 240 scfm (Figure 3).

l. Air Dryer Afterfilter (AF-1)

Pall Trinity Model MEC100-6EC32, 6-1/2-inch OD by 30-inch length, 1-1/2-inch NPT connections, 6 cartridges (3 lines of 2 each).

This filter was provided to remove desiccant particles that might be carried out of the dryer.

m. Air Surge Tank (V-1)

Van-Air Model V20-80-200, vertical coded pressure vessel, 200 psig rated, 80-gallon capacity, welded steel,

20-inch diameter by 72-inch height. This tank was selected to provide a surge volume downstream of the dryer to smooth out pressure fluctuations caused by the dryer regeneration cycles.

n. Pressure Reducing Valve (PC-1)

Mason Neilan Model 11-12, 1-inch NPT, 2 to 40 psig control range, bronze. This valve is designed to allow the high pressure (100 psig) dry air from the surge tank to flow to the ozone generators at a controlled lower pressure (10 to 12 psig).

o. Ozone Generators (OZ-1, OZ-2, OZ-3, OZ-4, OZ-5, OZ-6)

CPAC Model OZ-144-H. CPAC's Model OZ-144-H was selected as the ozone generation equipment for the plant. The basic dielectric cell used is the flat-plate Lowther type (Reference 3) (see Figure 13), which is a sandwich made up of an aluminum heat sink, a steel electrode coated with a ceramic dielectric, a glass spacer which provides the corona discharge gap, a second ceramic coated electrode fitted with inlet and outlet ports, and a second aluminum heat sink.

The individual cells are sandwiched into bundles or modules of 30 cells each. Each 30-cell module has a nominal ozone output capacity of 1 pound per hour but, at maximum efficiency, will usually produce about 10 percent more. The design requirement of 150 pounds per day was fulfilled by using six of the 30-cell modules, which are individually powered and controlled. With the option of using only one, two, or any combination of the modules up to six, a wide operating flexibility is available. In addition, each individual module may be operated at any output level from approximately 25 to 100 percent (see Figure 4).

p. Reactor Gas Feed Rotameters (F-1, F-2, F-3)

Fischer Porter Model 10A3565A, glass tube, stainless steel floats. The Houston Research report recommended a gas distribution of 80:12:8 percent to be fed to each of the three reactors R-1, R-2, and R-3, respectively.

The F-1 rotameter was designed to indicate gas flows to the first reactor in the range of 50 to 80 percent of total gas flow. F-2 and F-3 were designed for a range

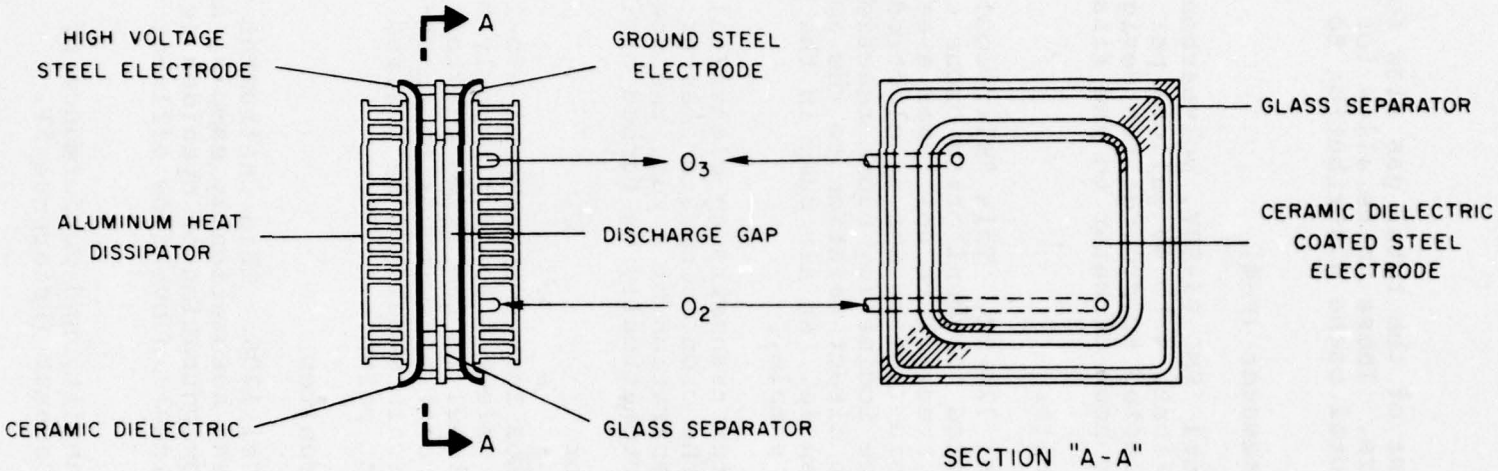

Figure 13. Ozone Generator Cell (Lowther Type)

of 5 to 25 percent of the total gas flow for the second and third reactors. These units allow for considerable flexibility in total ozone distribution to the three reactors.

q. Water Rotameter (F-4)

Dwyer Model RMB-84-SSV, polycarbonate tube, stainless steel float, 4 to 40 gallons per hour. This rotameter was selected to provide the design flow rate of 25 gallons per hour of water to the first reactor.

r. Ozone Monitor

Mast Model 724-2M. This "microcoulomb ozone sensor" was selected for monitoring ozone concentration in the operating area. This unit uses a sensing solution containing potassium iodide and an electrode chamber where generation of free iodine (by ozone reaction with KI) causes a current flow in direct relation to the amount of ozone present in the sample. An air pump in the unit draws a continuous fresh sample.

The monitor transmits an electrical signal to a microammeter on the ozone generator master control panel. At an ozone concentration of 1 ppm, the power to the generator will automatically be turned off.

s. pH Monitor

Great Lakes Instruments Model A70-1 with Model P60L-4 probe was selected to continuously monitor and indicate the pH level in the third reactor. The instrument is equipped with control switches to start-and-stop the addition of chemicals should it be desired to control the pH at some set point.

t. Cyanide Monitor

Orion Model 1206. This instrument was designed to continuously and automatically sample, analyze, indicate, and record the concentration of cyanides (except for complexed iron cyanides) in overflow effluent from the No. 2 Reactor.

The reliability and performance of this device was reported by Bennett (Reference 5).

A sampling pump (Jabsco Model 17020) circulates liquid between the No. 2 Reactor overflow line and the cyanide monitor to continuously provide a fresh sample of solution to be analyzed.

SECTION III

ASSEMBLY AND INSTALLATION

Except for the ozone generators, equipment and components were delivered directly to Tinker AFB.

The ozone generators were assembled and tested at the contractor's manufacturing facility. After testing, the three consoles were shipped individually to Tinker AFB.

1. EQUIPMENT ARRANGEMENT (See Figure 14)

Building No. 3514 at Tinker AFB is a conventional concrete block structure that formerly housed equipment for chlorination treatment of cyanides. After removing several gas cylinder feeding stations and one small tank from the central equipment room, a cleared space approximately 20 by 40 feet was available for the new installation.

The optimum equipment arrangement for both operating and maintenance accessibility resulted in the air preparation and ozone generator systems being located in a line along the south wall of the room, the waste surge tank at the west end, and the cyanide reaction system along the north wall.

When practical, major equipment components were left on shipping skids, as requested. Because of the vigorous agitation and the large weight of liquid involved, however, the mounting legs of the reactors were placed on pads made from pieces of 4-inch angle iron which were, in turn, bolted to anchors in the concrete floor.

The reactor vent system fan is mounted on the north wall above the cyanide monitor at an elevation of 10 feet with the discharge line extending through the wall. The main exhaust duct (PVC) extends along the north wall above the reactors and is supported from roof structural members. Vent lines to each reactor drop vertically from the main duct.

2. PIPING SYSTEMS

In general, standard black iron piping and fittings were used for all air lines, while PVC materials were used for cyanide and ozone lines.

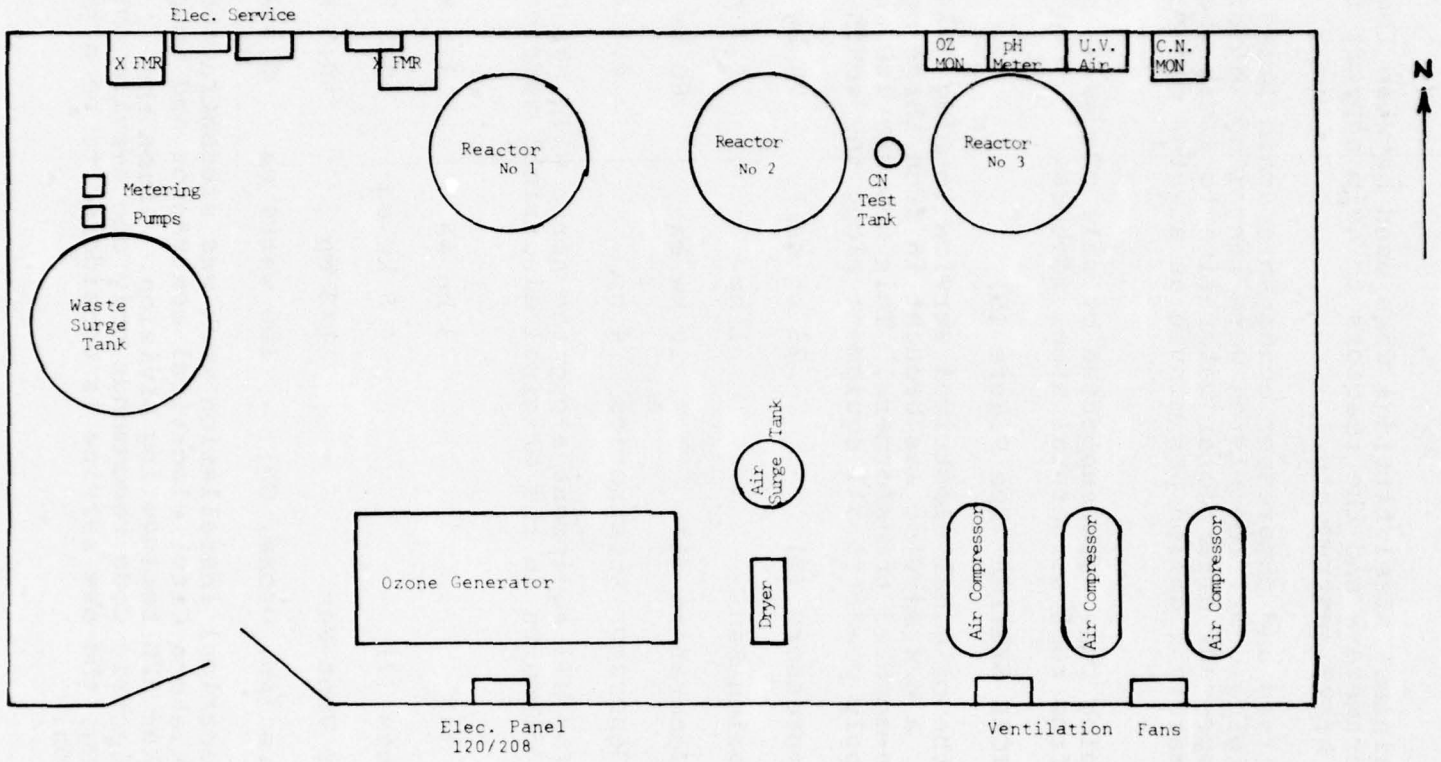

Figure 14. Equipment Layout

Stainless steel fittings were used between the gas feed rotameters and the reactors to help support these relatively heavy instruments.

Water lines and compressor condensate drain lines are also PVC piping. Orifice plates were installed in unions on each compressor aftercooler water line to limit the flow to approximately 1 gallon per minute as a water conservation measure.

All piping runs were supported by wall clamps or hangers suspended from roof structural steel members.

3. ELECTRICAL SYSTEMS (See Figure 15)

Since the original electrical service to Bldg 3514 was inadequate, a new service was brought in from three new 50 kva pole-mounted transformers. This new service was used to supply power to all equipment along the south wall.

Air Compressors (3)	25 hp ea	70 kw
Ventilation Fan	1 hp	1.1 kw
Ozone Generators (6)	10 kw ea	60 kw
Ozone Generator Accessories	4 hp	4.4 kw

Power for all equipment along the north wall was obtained from spare circuits in the original electrical service panels.

Mixers (3)	3 hp ea	9.0 kw
UV Lights (2)	4.5 kw ea	9.0 kw
Reactor Vent Fan	1/3 hp	0.5 kw
Monitors (pH, Ozone, CN)	100 watts ea	0.3 kw

All electrical installation work was subcontracted to a local (Oklahoma City) electrical contractor and inspected by the Tinker AFB Engineering Division. Since the National Electric Code recommends only one service entry per building, the new service is considered to be a temporary installation.

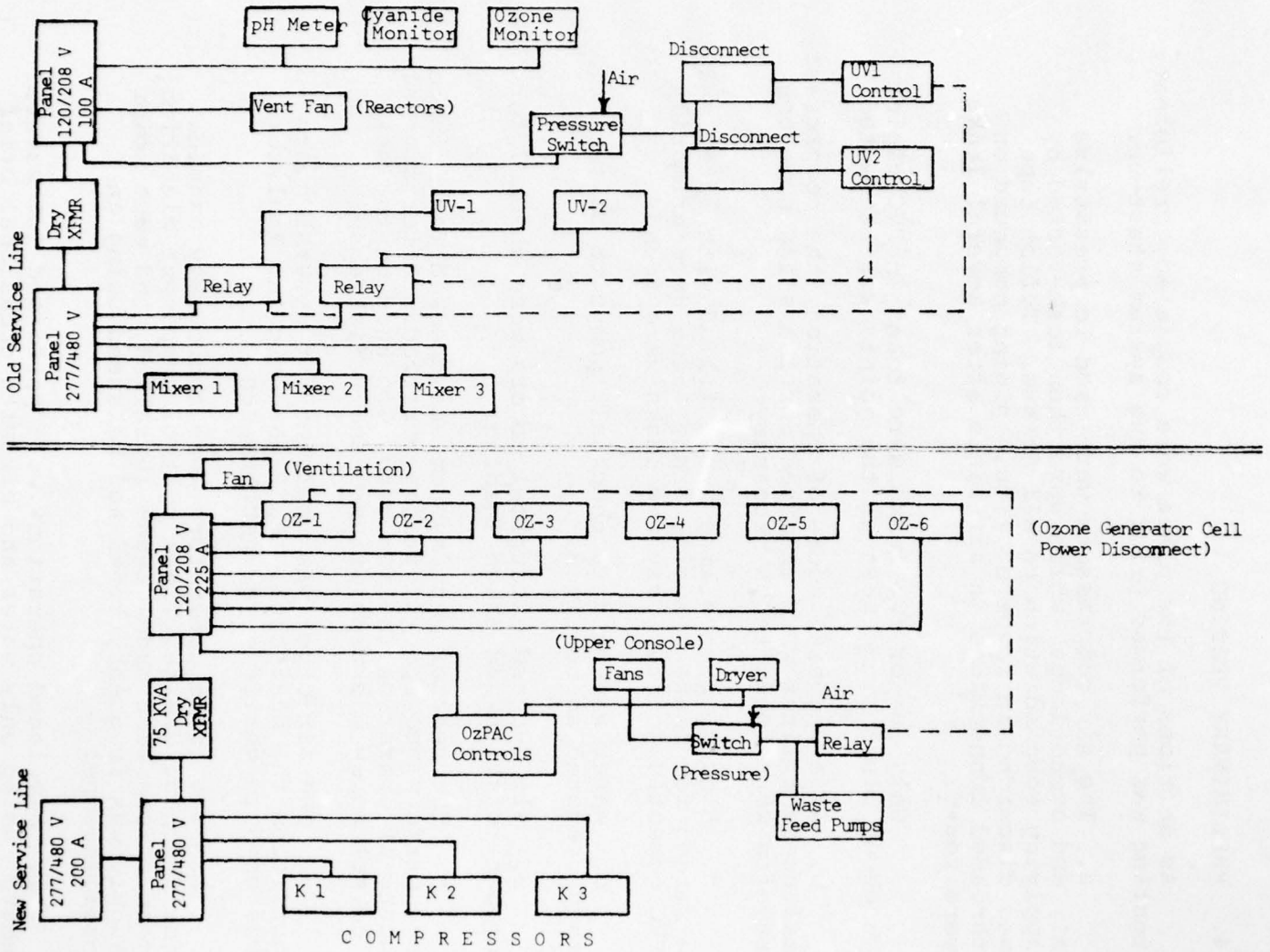

Figure 15. Electrical Service Schematic

4. PRELIMINARY TESTING

As sections of the plant were completed, preliminary testing was performed prior to the system start-up.

a. The air compressors were used to pressurize air and ozone lines, which were then leak-tested by applying soap solution to all joints. Teflon tape was discarded in favor of liquid piping compound on threaded connections in air lines after several leaks were found.

Only one or two leaks were found in PVC piping on ozone lines since most of the joints were cemented.

b. After several hours of operation, the compressor oil coolant lines were examined for leaks and numerous repairs were found to be necessary.

c. Liquid process lines were filled with water and examined for leaks. Again, since these were primarily PVC cemented joints, very few leaks were found.

d. Water was used to check all pumps to be sure they operated as required.

e. All 3-phase electrical motors were checked for proper rotation and phase loading.

f. The reactor vent system was checked for balance and performance specifications verified. After several hours of operation the fan rotor loosened on the shaft. The set screw was repositioned and retightened.

g. The air dryer was operated for several hours to condition the desiccant. An Alnor Dewpoint Analyzer was used to verify dryer performance.

h. The ozone generators were thoroughly examined for shipping damage, final control component electrical connections were made, fuses installed, and each power supply was frequency tuned and balanced using an oscilloscope.

i. Simulated operations were performed for several hours, using only water and air with occasional brief applications of power to the ozone generators to check all electrical, mechanical, and safety control elements of the plant before treatment of cyanide waste was attempted.

SECTION IV

PERFORMANCE TESTING

1. EQUIPMENT OPERATION

a. Waste Transfer Pump

By level difference in the waste surge tank before and after making a transfer, it was determined that 630 gallons were pumped in 1 hour and 15 minutes. Pumping rate was 8.4 gpm.

b. Waste Feed Pumps

To accurately determine the pumping rate, the feed line was disconnected at a pipe union where the line enters Reactor R-1 and cyanide waste was collected in a calibrated plastic container as it was pumped through the line. By collecting liquid in 10-minute intervals and adjusting the pump output calibration screw, each pump was set to deliver 6.25 gallons per hour.

c. Air Dryer

During the conditioning period and at the beginning of several performance runs, the performance of the dryer was measured by use of a dewpoint meter. Tests were made on air after passing through the ozone generators (with no power on) by using a sampling valve in the gas feed line to Reactor R-1. Immediately after start-up, the dewpoint was usually in the -20°to -30°F range. After 10 or 15 minutes of operation, the dewpoint was maintained in the -40°to -50°F range.

d. Ozone Generator

Immediately after assembly and prior to shipment, each individual 30-cell unit was tested and ozone output measurements were made at approximately half-power levels. Procedures for measuring output are described in Appendix A.

Results of these tests indicated an average output of 257.5 g/hr for an average power input of 5345 watts.

Collectively, this was 3.4 lbs/hour of ozone at a power level of 32,000 watts (20.75 watt-hour per gram)

and compared favorably with design specifications of 6.25 lbs/hour at 57,000 watts (21 watt-hour per gram). In numerous installations of this type of ozone generator, the contractor has determined the optimum output/power ratio to be consistently in the range of 1 g/20 watt-hours ±10 percent.

After installation at Tinker Air Force Base, additional ozone output tests were run at various power levels. These results are shown graphically in Figure 16 and indicate that actual ozone production rates were within the design range. At higher air flow rates, in which the delivered ozone concentration would be between 0.5 and 0.75 percent rather than 1 percent, output rates above the design level could be generated.

Performance of automatic safety controls was also confirmed during the testing period.

- Ozone was intentionally leaked into the operating area on several occasions and the effect on the ozone monitor was observed. Increasing ozone concentrations were indicated on the microammeter on the master control panel and at the set point of 50 microamps (equivalent to 1 ppm of ozone as measured by the Mast Meter), all power was automatically shut off to the generator cells and the cyanide feed pump.

- The low air pressure shutdown control was frequently tested at the end of performance runs. This was achieved by shutting off the air compressors and allowing the pressure to drop as the air continued to flow from the various surge tanks to the ozone generator. As soon as the pressure fell below 45 psig, as indicated on the dryer pressure gauges, power was shut off to the generator cells and the cyanide feed pump.

- To test the thermal switches in each of the six ozone generator cell modules, power was temporarily disconnected to the cooling fan. With the power at a level of 20 amps, it took 3-1/2 to 4 minutes for the cell temperature to reach the shutoff level of 200°F, at which point the thermal switch shut off power to the cell module being tested.

Within a few minutes, the cells cooled and it was possible to turn power back on.

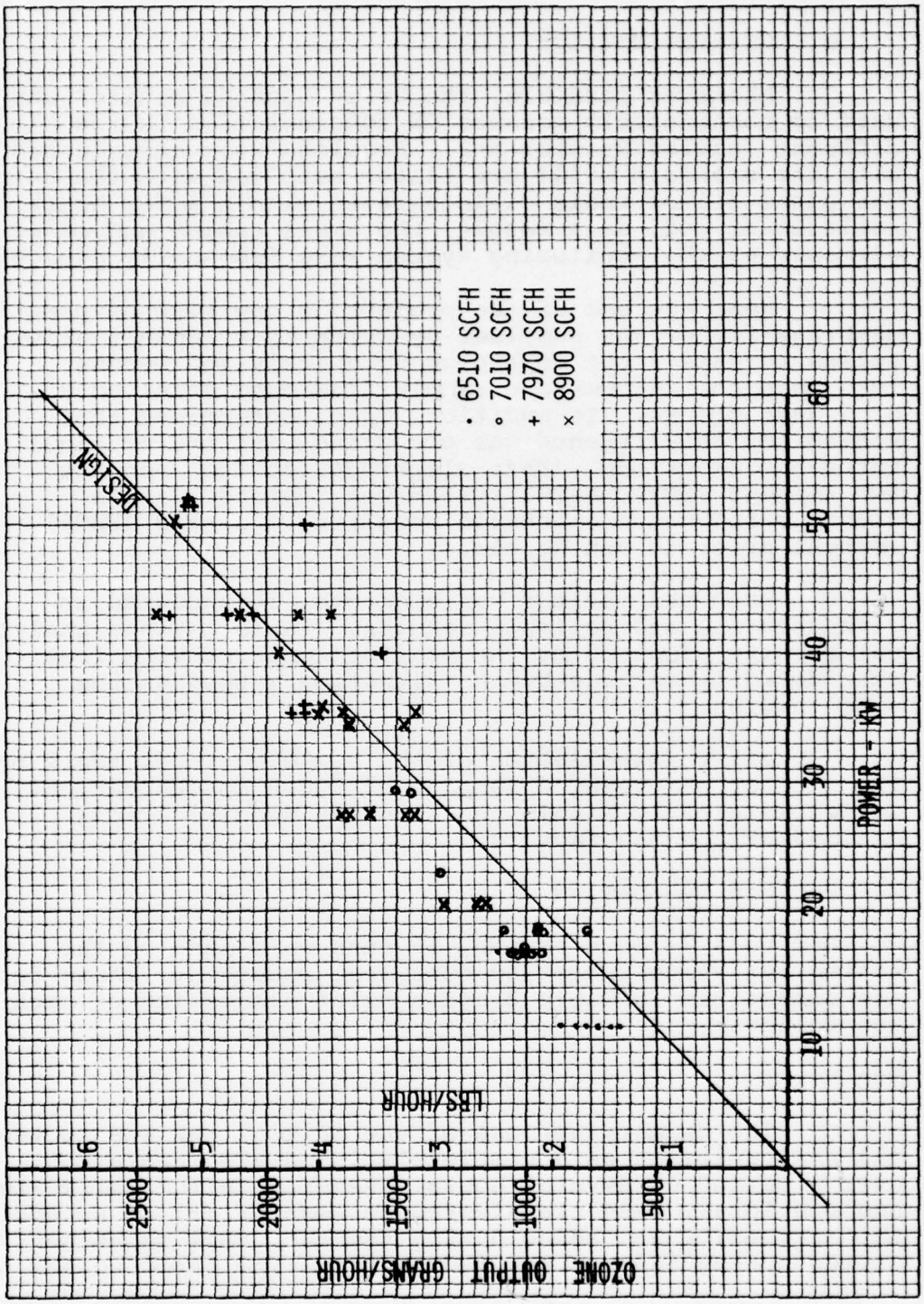

Figure 16. Ozone Output Test Data

e. Cyanide Monitor

Whenever possible, the Orion Cyanide Monitor was used to continuously measure CN concentration in the effluent leaving Reactor R-2. Problems were experienced with the standard millipore filter supplied with the unit. The paper filter media disintegrated within a few hours of replacement and, as a result, the small tubing and other elements of the monitoring system were frequently plugged.

Near the end of the project, a new type of plastic membrane filter was supplied by Orion that doesn't allow solids to pass - but does plug up quickly and passes less than the recommended sample flow rate after only 2 or 3 days of use. In addition, Orion determined that sodium ion interference was occurring with the original reference electrode. That electrode (sodium) and its two reagent (EDTA, NaOH) system was replaced with a fluoride reference electrode requiring a single (EDTA) reagent prior to Run No. 13.

When the monitor was operable, it appeared to give accurate and reliable results. Table 1 lists analytical results produced by the monitor compared with free cyanide analyses made by the titration method on the same samples.

After installation of the new electrode, tests by the monitor on prepared samples of known concentrations were consistently within the accuracy specifications claimed by the manufacturer.

2. PROCESS EVALUATION

During a 3-month period, 15 runs were made on the system for which operating data were recorded. These data are summarized in Table 2 and a brief discussion of each run follows:

Run No. 1

The primary purpose of the initial run was to test all the equipment as a completely integrated operation over a period of several hours. Several gallons of waste had previously been transferred to Reactor R-1 so no additional cyanide was added during the run. All ozone generated during the run was fed to R-1. The gas feed and

TABLE 1. CYANIDE MONITOR RESULTS
vs TITRATION PROCEDURE RESULTS

Sample			CN - mg/l	
Date	Time	Location	Orion Monitor	Titration (Free CN Only)
9/20	17:00	Reactor R-2	240[a]	263
9/20	17:00	Reactor R-3	0.45	Approx 6.0
9/20	23:00	Reactor R-2	640[a]	654
9/21	04:30	Reactor R-2	900[a]	922
7/27	10:00	Reactor R-2	0.3	Approx 3.0
7/27	10:00	Reactor R-3	0.75	Approx 2.3

a. Samples were diluted with distilled water using a graduated cylinder for measurements in order to stay within the 0 to 100 mg/l scale on the monitor.

dispersion system appeared to function well, resulting in a good foam blanket about 10 to 12 inches thick on top of the liquid (Figure 17). No ozone was detected (by smell) in the reactor offgas.

With an ambient air temperature above 90°F, the room ventilation system appeared to be inadequate for removing the heat load from the air compressors and the ozone generators. The room temperature rose to 110°F and the compressor circuit breaker, in the power distribution panel, tripped several times.

Run No. 2

After removing a window to improve ventilation in the operating area, the system was again turned ON at a moderate ozone generator power level. No additional cyanide was added to the system and most of the ozone was fed to Reactor R-1. A small amount of ozone was fed to R-2 which was about half full of liquid (water plus overflow from R-1). Heat build-up problems continued, so after this run, the room exhaust fan was relocated to a higher

TABLE 2. RUN DATA SUMMARY

Run No.	Duration (Hours)	Ozone (Lbs)	Cyanide (Lbs)	H_2O (Gal)	Ozone Distribution (Percent)			Cyanide Concentration (mg/l)		UV Lights ON (No.)	Remarks
					to R-1	to R-2	to R-3	Effluent	Feed		
1	3.75	11.3	None	None	100	-	-	None	-	-	-
2	4	9.7	None	None	93	7	-	None	-	-	-
3	4.5	8.3	2.8	90	84	16	-	None	14,100	-	-
4	9.5	13.1	6.3	60	84	14	2	50	14,100	-	-
5	9	15.5	5.6	105	78	15	7	42	14,100	2	-
6	8	18.2	5.6	105	78	15	7	36	14,100/21,800	1	R-2 Spargers Plugging
7	14	38.6	15.3	305	85	9	6	-	21,800	1	R-2 Spargers Plugged
8	6	14.6	6.9	140	85	8	7	-	21,800	1	New Spargers in R-2
9	9.5	29.2	9.2	235	82	13	5	113-116	21,800	1	All Spargers Plugging
10	23	74.6	21.7	410	71/69	22/23	7/8	228-208	21,800	1	New Sparger Design
11	49.5	159.8	56.0	620	68	23/21	9/11	217-173	24,700	1	-
12[a]	19.6	19.7	None	None	_	57/33	43/67	288-142	-	2	Batch Run on R-3
13	71.5	316	91.6	1150	62/80	25/12	13/8	205-348	35,300	2	-
14	83	374	134.5	1950	73/64	19/28	8	448-372	35,300	2	Modified Spargers in R-1
15[b]	14	13.5	None	None	76/50	9/8	15/42	316-236	35,300	2	Batch Run on R-3 with pH Adjustment

Ceramic spargers were used in Runs 1 to 9. PVC pipe spargers were used in Runs 10 to 15.

a. During run pH level dropped from 12.2 to 10.4.

b. During run pH level rose from 7.4 to 8.6.

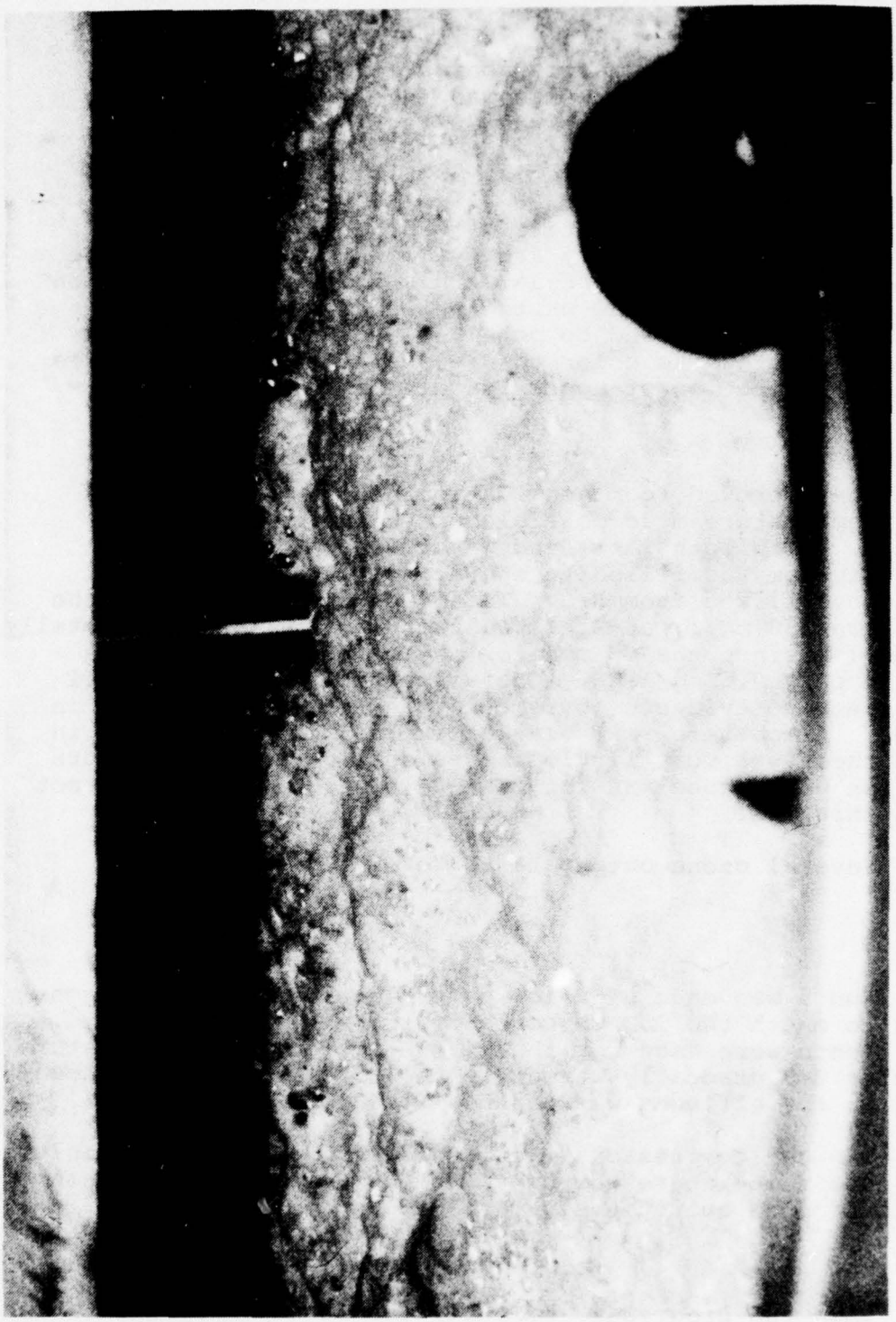

Figure 17. Foam in Reactor R-1

elevation in the wall directly above the air compressors. Room temperature during the run was in excess of 105°F when the outside temperature was 90°to 95°F.

Run No. 3

Shortly after the start of Run No. 3, the liquid in R-1 changed color rapidly from yellow to green and ozone could be detected in the offgas. This indicated a depletion of free cyanide so cyanide waste feed and water feed were turned on. Ozone was fed to both R-1 and R-2. Sample analyses indicated the color change seems to occur at a free cyanide concentration of approximately 10 to 15 mg/l.

Run No. 4

The improved room ventilation and low (75°to 80°F) ambient temperature made possible an uninterrupted run of 9.5 hours. With both waste and water feeds ON, the entire reaction system was filled to operating level and some effluent overflowed from R-3. Total CN concentration in the effluent was 50 mg/l, and this was assumed to be almost totally iron complex since the CN monitor indicated liquid leaving R-2 to be only 0.5 mg/l CN. Gas dispersion was good in all reactors and no evidence (by smell) of ozone was observed in offgases. A moderate foam blanket (2 to 3 inches) formed in R-2 but there was very little in R-3 during the last 2 hours of the run when ozone was fed to R-3. The UV lights were not used on this run.

Several ozone output tests were made at low power levels.

Run No. 5

Run 5 was made at a low power level on all ozone generators to match the low CN concentration in the waste feed. The UV lights were used for the first time and the temperature in Reactor R-3 gradually warmed up to 135°F. Total CN concentration in the effluent was reduced to 42 mg/l.

The air compressor circuit breakers again gave problems as the room temperature warmed up to 110°F during the afternoon. Additional ozone output tests were made.

Run No. 6

This run progressed smoothly for about 6 hours at which time the gas feed rate to Reactor R-2 began to drop off.

It appeared that the gas spargers were plugging. Only one UV light was used in order to hold the temperature down around 135°F in R-3. The final effluent had a total CN concentration of 36 mg/l.

It may have been coincidental to the sparger problem, but a new tank of raw waste was transferred to the surge tank and was initially fed to the system during this run.

During this run, representatives of compressor manufacturers and the electrical subcontractor determined that inadequate (50 amp) circuit breakers had been installed in the power distribution panel to the compressors.

Run No. 7

Several weeks elapsed between Runs 6 and 7 during which time heavier (70 amp) circuit breakers were installed for the air compressors and a second ventilation fan was installed to aid in removing heat from the operating area.

The reactors were full of liquid during the shutdown period and there was no evidence of restriction to gas flow in R-2 at the start of Run 7. As the run progressed, however, the flow again dropped off and sparger plugging was confirmed.

Except for the R-2 sparger plugging problem, this run went smoothly for 14 hours at 50 percent of ozone generator power capacity and continuous waste feed with a CN concentration of 21,800 mg/l. Only one UV light was used. For most of the run, the CN monitor results showed a concentration less than 1 mg/l in R-2 effluent, again indicating apparent destruction of all except complexed iron cyanides.

There were no compressor circuit breaker problems during this run and heat removal from the operating room was greatly improved.

Subsequent to the end of Run 7, the R-2 Reactor was emptied to the outside effluent receiver tank, the spargers were replaced with new units, and the reactor was refilled with water.

The plugged sparger tubes appeared to be coated on the inside with a gray-white solid material that was soluble in acid and believed to be a carbonate.

Run No. 8

This was a short run made primarily to reestablish equilibrium conditions in the reactor system. No samples were taken.

Run No. 9

During this run an attempt was made to run only half of the ozone generators, but at full power. As the ambient temperature increased during the day, the circuit breakers on the power distribution panel started kicking out. Further investigation revealed that these breakers were also undersized and plans were made to replace them.

Four ozone generators were operated at 75 percent of full power for most of the run. Samples of final effluent were still below 1 mg/l in free cyanide but over 100 mg/l in total cyanide. Toward the end of the run, spargers in all reactors appeared to be plugging with those in R-3 almost completely plugged.

Subsequent to the end of Run 9, new spargers were installed in all reactors. These spargers were fabricated using 18 inch lengths of 1/2-inch PVC pipe with 1/16-inch holes drilled on 1/4-inch centers. The 1/16-inch holes were expected to pass the apparently small sized solids which plugged the ceramic units. Although the small pore size of the ceramic units appeared to give the desired liquid-gas contacting efficiency, it was felt necessary to sacrifice some of that efficiency to prevent plugging.

To conserve reaction system liquids, R-3 liquid was pumped out to the effluent receiver tank, R-2 liquid was transferred to R-3 after the spargers were changed, R-1 liquid was pumped to R-2 after those spargers were changed, and R-1 was filled with water after its spargers were replaced.

Run No. 10

As expected, the new sparger units produced gas bubbles of a larger size and the foam blankets on R-1 and R-2 were reduced in thickness to about 25 percent of what they had been with the ceramic units. In addition, ozone could be detected by smell in the Reactor R-1 offgas. At first, this was believed to be a result of the low cyanide concentration (R-1 contained water at

the start of the run) in the Reactor but the situation did not change as the run progressed.

A larger proportion of ozone was fed to R-2 and R-3 in an effort to reduce the loss from R-1 and to see if some of the reaction load could be shifted to the other two.

The run was discontinued after 23 hours because it was discovered that the waste feed pump had been accidently shut off after about 18 hours. The ozone monitor then automatically shut off the OzPACs when it detected the increased concentration of ozone being vented.

Total cyanide concentration in samples of the treated effluent were in excess of 200 mg/l although the CN monitor again indicated results less than 1 mg/l in R-2 effluent. Accuracy of the monitor was questioned and the manufacturer was consulted. The manufacturer subsequently advised that modifications to the monitor would be necessary.

Run No. 11

After reestablishing the CN concentrations in the reactor system, a prolonged run of 49.5 hours was made. Again, in an effort to reduce the loss of ozone from Reactor R-1, the gas feed rates were set to shift more of the reaction load to R-2 and R-3. The percentage of total gas feed to each reactor (in order) was 68-21-11 versus the original design criteria of 80-12-8. In addition, the water feed rate to R-1 was reduced to increase the cyanide concentration as a means of improving the reaction rate. Some ozone could still be detected in the R-1 offgas.

Free cyanide destruction appeared to proceed as expected, as evidenced by the solution color in the reactors (and later verified by sample analyses) but, using one UV light, the total cyanide concentration in the final effluent was only reduced to 240 to 260 mg/l. After turning on the second UV light for the last 5 hours of the run, this concentration was reduced to 173 mg/l.

The CN monitor was out of service during this run.

Run No. 12

Since the reaction system was not producing an effluent of the desired quality, Run 12 was designed to obtain rate information on the decomposition of the complex cyanides in Reactor R-3. Prior to making the run, the UV light wells were removed from the reactor and cleaned of the hard gray-black scum that had gradually built up.

A batch run in excess of 19 hours was made in which ozone was fed and no transfer of liquid occurred between reactors. Water was added occasionally to R-3 to replace evaporation losses. Both UV lights were used.

Figure 18 shows the rate at which cyanide concentration was reduced during the run. During the early hours of this run, a higher rate of reaction was indicated in both R-2 and R-3, presumably due to the presence of free cyanides. A solution color change was observed in R-2 as additional verification of initial free cyanide presence. Subsequently, the reaction rate appeared to be constant. Total cyanide concentration in R-3 was 142 mg/l at the end of the run. No attempt was made to adjust pH which gradually decreased from 12.2 to 10.4. Temperature gradually increased to a high of 147°F at the end of the run.

Run No. 13

Prior to this run, heavier power panel circuit breakers for the OzPACs were installed and a more highly concentrated batch of waste was received. This enabled the entire system to be operated at a higher capacity level than previous runs. The equipment operated smoothly and continuously for a period of 3 days during which final output tests on the ozone generators were completed.

The CN monitor was returned to service after modifications to the sampling filter and to the electrode measuring system. The filter plugged within a few hours but the measuring system appeared to work well.

Loss of unreacted ozone from Reactor R-1 was again very evident in spite of the higher waste feed concentration and higher ozone-in-air feed concentration. Various combinations of water feed rates and feed gas distribution among the reactors were tried but the best final effluent quality obtained was still in excess of 200 mg/l total

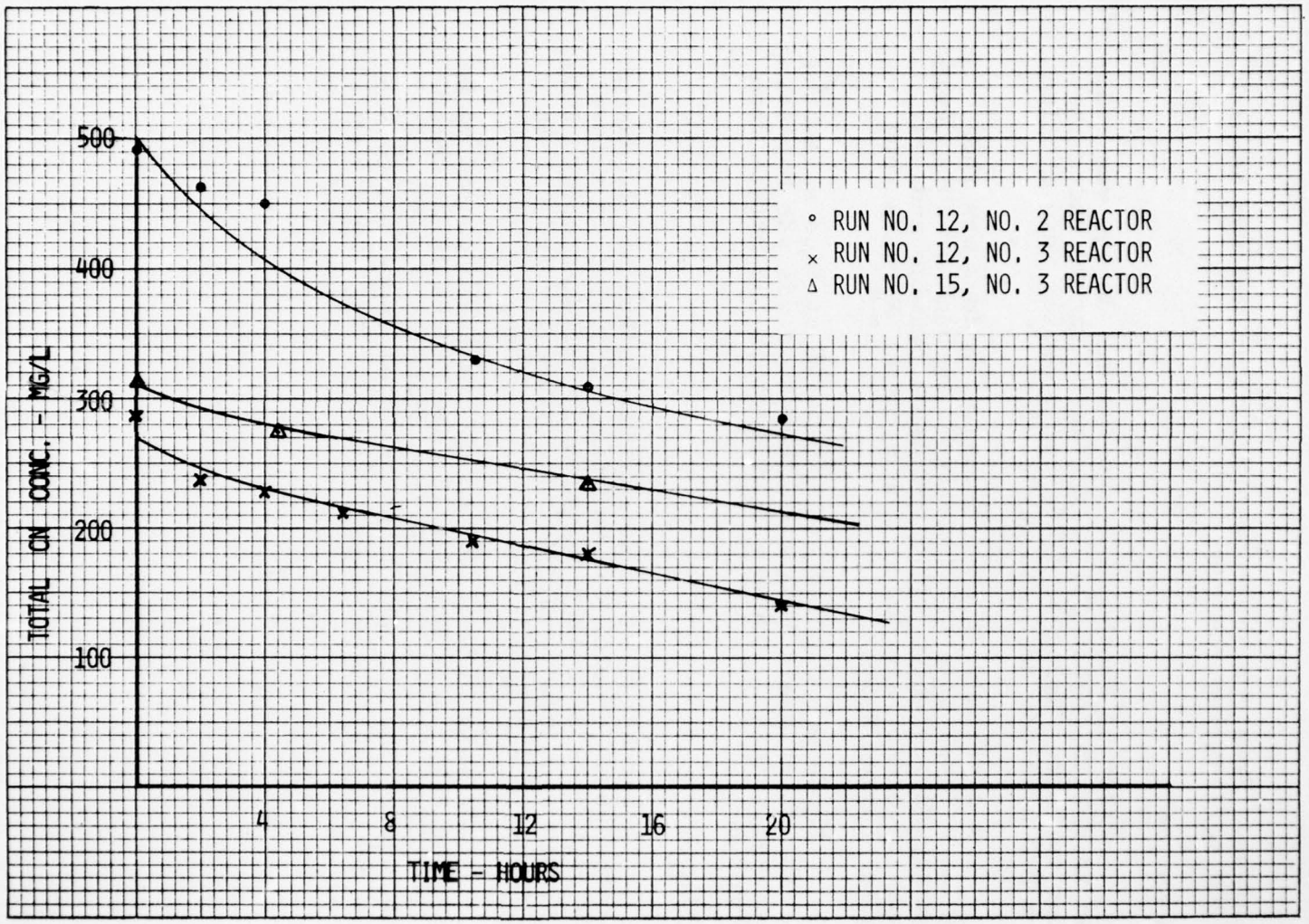

Figure 18. Total Cyanide Concentration Versus Time

cyanides. Free cyanide concentration in R-2 was as high as 800 mg/l during the run.

Run No. 14

Prior to Run No. 14, the sparger design was modified in R-1 to inject all of the gas directly under the mixer turbine. Holes of 1/16-inch diameter were drilled in a PVC pipe cap as a sparger device.

A continuous run in excess of 3 days was then made at a level of approximately 75 percent of full design capacity during which 134.5 pounds of cyanide and 374 pounds of ozone were fed to the system. Results were similar to Run No. 13.

Large gas bubbles and excessive surface splashing near the mixer shaft indicated that some gas was bypassing the mixer turbine. Ozone was present in the offgas from Reactor R-1.

Run No. 15

A batch run was made similar to Run No. 12 except that the pH in Reactor R-3 was first adjusted to a level of 7.4 (from 9.8) by the addition of sulfuric acid. Both UV lights were used and the temperature leveled out in the range of 150°to 155°F.

The rate of destruction of cyanide appeared to be about the same as in Run No. 12 (see Figure 18). Color of the liquid in R-3 changed from green to a muddy red-brown during the run while the pH level increased to 8.6. Total CN concentration dropped from 316 mg/l to 236 mg/l.

SECTION V

DISCUSSION AND CONCLUSIONS

Although operation of the plant to accumulate data was extended beyond the level of effort originally planned, the significance of the data and any interpretation thereof should be tempered with the following information about the operational characteristics of the system.

- -At the design level of operation, it takes a minimum of 39 hours to reach equilibrium in the system after any change is made affecting the No. 1 Reactor parameters.
- -A very large number of combinations of operating variables is possible, although efforts were made to maintain conditions similar to those reported to be successful.
- -Without the use of sophisticated equipment for continuously measuring and recording ozone losses in the offgas from the three reactors, it is not possible to calculate meaningful reaction rate information.
- -Each portable tank of waste material supplied to the plant (there were three used during the performance runs) contained material of widely different chemical and physical characteristics.

1. OZONE USE RATE

During performance runs, the rate of generation of ozone was controlled at a level believed to be sufficient for the CN concentration level in the particular batch of waste being used. With no accounting for ozone lost to the reactor vent system, the ozone used per pound of waste destroyed was calculated for portions of several runs. These are summarized in Table 3.

Data were obtained to calculate the ozone usage rate for only one of the runs (Run No. 6) in which the ceramic spargers were in service. In spite of the absence of ozone in the reactor's offgas, the efficiency of ozone use was apparently no better than the later runs using PVC spargers.

TABLE 3. CALCULATED OZONE USAGE RATES

Date	Run No.	Hours	Cyanide Feed (Lbs)	Cyanide Destroyed (Lbs)	Ozone Feed (Lbs)	Lbs/O_3 Per Lb CN Feed	Lbs/O_3 Per Lb CN Destroyed
7/29	6	6	5.45	4.87	17.8	3.26	3.6
8/24, 25	10	5.5	7.12	5.22	17.2	2.42	3.3
8/26	11	3.5	4.56	3.45	12.1	2.65	3.5
9/20	13	6	11.0	8.59	25.8	2.35	3.0
9/24	14	12	21.3	15.94	51.9	2.43	3.25
9/26	14	21.75	28.8	31.06	93.5	3.24	3.0

2. GAS-LIQUID CONTACTING

In any gas-liquid reaction system, the key to success is in the efficiency of the contacting devices.

Factors affecting that efficiency include gas bubble size, mixer design, hydrostatic pressure, decomposition rate of ozone, and partial pressure (gas solubility) of ozone. Considerable data on these factors were reported from previous studies by Garrison et al (Reference 2).

The original design for the system at Tinker Air Force Base using ceramic spargers (with a pore size to give 100 micron bubbles) and the flat blade turbine 3 hp mixer appeared to perform well until the spargers plugged. Although the mixer power input of 7.5 hp per 1000 gallons must be considered only a medium level for Reactor R-1 (but more than adequate for R-2 and R-3), the use of any higher power input is believed to be unfeasible because of the proclivity of the waste to foam excessively.

The PVC pipe spargers with 1/16-inch holes, however, did not perform well even when limited to an area directly under the mixer turbine in No. 1 Reactor. The volume of gas being fed to the first reactor is too large to be limited to any small percentage of the cross-sectional area of the vessel.

Since the presence of solids is a problem that apparently cannot be avoided, a new gas-liquid contactor design that can tolerate the solids and still produce small gas bubbles must be developed.

3. SOLIDS FORMATION

Solids formed in all three reactors during performance runs in varying quantities, apparently related to the waste feed characteristics. Table 4 lists results of filterable solids analyses performed on random 250 ml samples.

These solids are settleable but do not accumulate in the reactors because they are kept in suspension by the mixers and move out through the overflow lines. The solids were identified as carbonates of the various metals in the waste and can be eliminated by acidification. Some of the plugged ceramic spargers were cleaned by soaking in an HCl solution.

TABLE 4. REACTION SOLIDS ANALYSES

Run No. 11	Filterable Solids
8/27/75	R-1 136 mg/l R-2 136 mg/l R-3 215 mg/l
Run No. 14	
9/25/75	R-3 2570 mg/l
9/26/75	R-3 1120 mg/l
Run No. 15 (Batch Run-pH Adjusted)	
9/28/75	R-3 2800 mg/l

All solids reacted with dilute HCl accompanied by gas formation and were believed to be carbonates.

4. WASTE CHARACTERISTICS

As operations progressed at Tinker Air Force Base, it became apparent that each batch of nickel strip waste delivered to the treatment plant was different. Analyses performed on the three batches used are listed in Table 5. Metals analyses were done on an AA spectrophotometer using Standard Method 129A (Reference 6). The amount of nickel cyanide in the waste was lower than anticipated and the concentration of iron cyanide was proportionately greater. If this high iron content continues to be characteristic of the waste, Reaction R-3 may have to be operated at a controlled pH much lower than its natural level to aid in breaking the iron complex.

Until considerably more experience is gained in identification of all characteristics of the waste that might have an effect on the selection of optimum operating parameters, it is not possible to draw many valid correlations and conclusions from the performance data collected during this contract period.

TABLE 5. RAW WASTE ANALYSES

Portable Tank No. 1	13,300 mg/l Free CN
pH 12+	14,100 mg/l Total CN
Portable Tank No. 2	23,900 mg/l Free CN
pH 12+	25,200 mg/l Total CN
Portable Tank No. 3	41,600 mg/l Free CN
pH 12+	42,000 mg/l Total CN
Mixture of Tank 2 and 3	33,100 mg/l Free CN
pH 12+	35,300 mg/l Total CN
	320 mg/l Iron (total)
	240 mg/l Silver
	260 mg/l Nickel
	640 mg/l Cadmium

5. FREE CYANIDE DESTRUCTION

Performance data appear to confirm the laboratory work done regarding ozone destruction of free cyanides. During the earlier runs, nearly complete free CN destruction in Reactor R-1 was indicated by the greenish color of liquid in Reactor R-2. Any time the free CN concentration in R-2 rose above 10 to 15 mg/l, the liquid became yellow in color.

Ozone usage rates shown in Table 3 are calculated on a total cyanide basis and are, of course, uncorrected for unreacted ozone losses in offgas. Assuming more efficient gas contacting equipment will be installed, the destruction of free cyanides in the first reactor should proceed as anticipated.

6. COMPLEX CYANIDE DESTRUCTION

Here, again, most of the complex cyanides appear to have been destroyed in the first two reactors, as predicted. The iron cyanide, however, proved to be very difficult to break down and, as indicated by the data in Table 2, remained in significant concentrations in the effluent from the third reactor.

The most concentrated waste used (Table 5) contained 2000 mg/l of complexed cyanides. In runs 13, 14, and 15, the final 300+ mg/l of CN proved very resistant to treatment. This material was analyzed and determined to be an iron complex. Since the raw waste originally contained 320 mg/l of iron, its presence in the final effluent is not surprising.

Special batch runs (No. 12 and No. 15) were made on No. 3 Reactor in which prolonged ozonation and UV light treatment only slowly decomposed the iron complex. These results are plotted on Figure 18 which shows that in Run No. 12, CN was destroyed at a rate of 7.5 grams/hour while, in Run No. 15, the rate was 8.0 grams/hour.

Even though the pH was adjusted down to 7.4 (from 9.6 on Run No. 15) the rate of decomposition of the complex was not significantly higher than from Run No. 13 where the pH was left at 9.8. In both cases, the ozone dosage rate was approximately 1 pound per hour per pound of CN initially present.

Although there is some probability that the solids formation on the outside of the UV light wells reduces the effectiveness of the lights, no definite proof of this was obtained.

The inability to break down the iron cyanides was the major reason for not achieving the contract goal of an effluent containing no detectable cyanides; however, it is also possible the effectiveness of Reactor R-3 to dispose of the iron complex was reduced in Runs 10 to 15 by an overload caused by the poor performance in R-1 and, in turn, R-2.

7. pH

The pH level of the raw waste used for performance runs was 12+. This level decreased on all runs except No. 15, as the material went through the reaction system, to a pH of 9.8 to 10.5 in the final effluent. During Run No. 15, on which the waste in R-3 was initially adjusted to a pH of 7.4, the pH rose to a final level of 8.6.

8. CYANATES

Table 6 lists the cyanate content of three different effluent samples. Although the concentrations for Runs 11 and 15 are considerably lower than anticipated, a partial explanation can be found in the large amount of ammonia gas that was released in Reactor No. 3. The distinctive smell of ammonia was evident any time the cover was opened on the reactor. Apparently, hydrolysis of cyanate was occurring, even at the alkaline pH levels present in R-3. The possibility of metals catalyzing the hydrolysis of cyanate has been reported by Hoffman (Reference 7).

TABLE 6. CYANATE ANALYSES

Run No. 11	8/27/75	R-3	12.6 mg/l
Run No. 14	9/25/75	R-3	7.2 mg/l
Run No. 15 (Batch Run, pH adjusted)	9/28/75	R-3	3.6 mg/l

9. CYANIDE MONITOR

When the cyanide monitor was operating, it was a very useful instrument. The continuous indication of cyanide concentration (except iron complex) in effluent from the No. 2 Reactor is very helpful in making timely adjustments to optimize operating parameters.

The monitor appeared to give entirely reliable results when the sampling system was not plugged, and the sample was being delivered to the analysis chamber as required. Keeping the sample filter functioning and the small diameter tubing lines open, however, proved to be difficult.

10. REACTOR SOLUTION COLOR

When the cyanide monitor was not operable, a less sophisticated, but effective, control monitor used was the color of solutions in the reactors.

In operation, as free cyanide is oxidized down to a near zero level, the original yellow color changes to green. The color comparison, then, between solutions in R-1 and R-2, can be used as a rough control indicator of how the reaction is progressing.

A photo (Figure 19) was taken of beakers containing (from left to right) raw waste, Reactor R-1 solution, Reactor R-2 solution, Reactor R-3 solution - no pH adjustment, and Reactor R-3 solution - reduced pH level. In the original colored slide from which this photo was made, the colors are quite distinctive: a dark amber, a clear yellow, a cloudy yellow-green, a darker cloudy green, and a cloudy red-brown.

Iron is probably responsible for the red-brown color of the pH adjusted solution from R-3.

11. ECONOMICS

Capital cost for ozonation plants to treat wastes containing 50 to 100 pounds per day of cyanides is in the range of $3000 to $3500 per pound of cyanide destroyed per day.

Operating costs on a dollar per pound of CN destroyed include:

Power (at $0.013 per kwh)	$0.68
Water (at $0.50 per 1000 gal)	0.03
Operating Labor (8 hrs)	0.64
Maintenance (2.5 percent/year)	0.22
Depreciation (13 percent/year)	1.14
Total	$2.71 per lb

Using data from an EPA report (Reference 10) published in 1971, the comparative costs of alternative methods of treating cyanide waste waters were calculated as shown in Table 7. The costs, as originally reported, were corrected upwards by a factor of 20 percent to allow for inflationary price increases to a current level.

Although capital costs are greater for the ozone method, operating costs are considerably lower than for the conventional chlorine method.

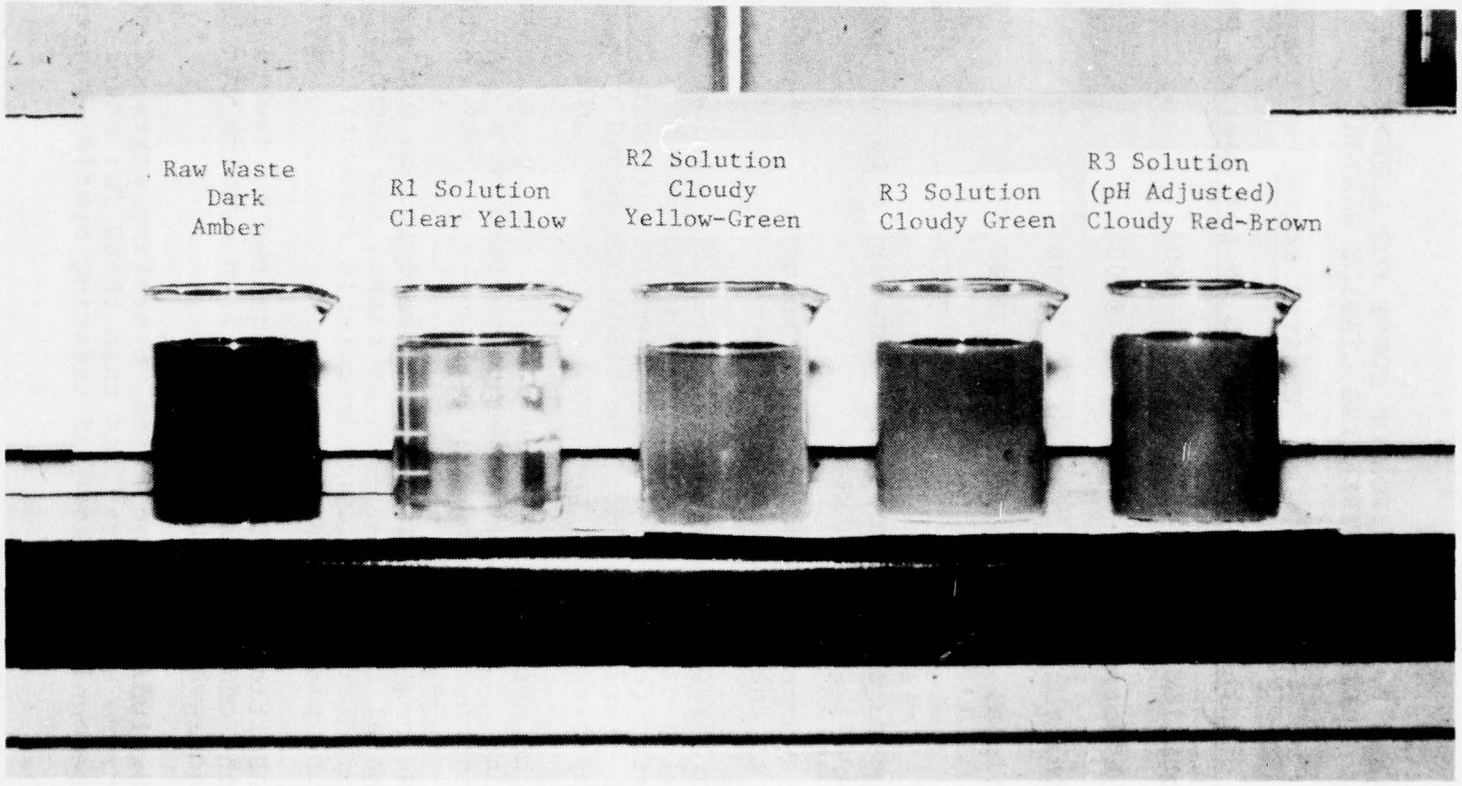

Figure 19. Color Changes in Reactor Solutions

TABLE 7. COMPARISON OF COSTS FOR ALTERNATIVE METHODS OF TREATING CYANIDE WASTES

Method	Capital Costs ($ per lb CN per day)	Operating Cost ($ per lb CN)
Ion Flotation	800	3.72
Carbon Adsorption	1400	2.20
Acidification-Volatilization	1700	3.29
Conventional (Chlorine)	1300	4.62
Ozone	3200	2.71

Costs based on experimental laboratory data and not on operational plant systems.

In summary, the following conclusions are offered in regard to the overall project:

- A large scale plant for treating cyanide wastes with ozone on a continuous basis can be constructed for an installed equipment cost of approximately $3000 to $3500 per pound of cyanide treated per day.

- The operation of such a plant can be automated and it can be expected to perform on a continuous basis for several weeks without shutdown.

- Successful treatment of free cyanides and most metal complexes, such as nickel and cadmium, is predictable to a nondetectable concentration in the plant effluent.

- Additional test work is required to assure that the complete oxidation of iron cyanide can be achieved in this plant.

- Excluding depreciation, operating costs of an ozone system are less than those for other recognized methods of treating cyanide wastes.

SECTION VI

RECOMMENDATIONS

The cyanide treatment plant, as installed at Tinker Air Force Base, should continue to be operated to dispose of all cyanide wastes generated on the base. Such operations should be closely supervised to obtain the maximum amount of additional performance data.

Some type of formal program, either in-house or by an outside contractor, should be scheduled as soon as possible to:

a. Develop a more efficient liquid-gas contacting device for use in the reactors.

b. Determine why the iron complex is not being completely decomposed, and possibly investigate the use of a more efficient UV light which was recently reported as being available.

c. Further study the operating variables in relation to waste feed characteristics to develop optimum performance parameters.

The potential for eventually using the cyanide monitor to automatically control the ozone generator power in relation to effluent cyanide concentration is sufficiently promising that its continued use is recommended.

The Air Force should consider installing similar treatment plants at other facilities where large quantities of complexed wastes must be disposed.

For future plant design, consideration should be given to:

- location of compressors in a protected (roofed) outdoor area to reduce ventilation (heat removal) problems in the operating area;

- addition of pH control equipment for Reactor R-3 with sufficient safeguards against the possible generation of HCN gas;

- design of reactors with a greater depth of liquid to increase hydrostatic head and contact time for improved gas-liquid transfer;

- design of easily removable spargers;

- possible use of filters to remove solids.

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APPENDIX A

TEST PROCEDURE

1. CYANIDE ANALYSIS

The Serfass (Reference 8) procedure for standard distillation was used to break down complexes for all total cyanide analyses. Figure A-1 shows the apparatus used. After conversion to free cyanides, the modified Liebig titration method (Reference 6) was used to determine concentrations.

2. OZONE OUTPUT - CHEMICAL METHODS OF ANALYSIS

a. Introduction

For the determination of ozone, a number of reactions have been used, such as that with ferrous iron (Fe^{+2}), manganous salts, ferrocyanide, arsenite, nitrate, and iodide. Iodide is the most convenient and is used almost exclusively.

In this procedure (Reference 9), a measured volume of gas containing ozone is bubbled through a solution of KI in water (2 percent by weight), which is adjusted to pH 7.0. The solution is then acidified to pH 2.5 with 7N sulfuric acid and titrated with 2N sodium thiosulfate pentahydrate ($Na_2S_2O_3.5H_2O$) to a starch endpoint.

The reaction of ozone with iodide appears to be the following (Reference 9):

$$O_3 + I^- \rightarrow O_2 + IO^- \qquad \text{(Fast)}$$

$$IO^- + H_2O \rightarrow HIO + OH^- \qquad \text{(Fast)}$$

$$HIO + 2I^- \rightarrow I_3^- + OH^- \qquad \text{(Slow)}$$

$$3HIO + 3OH^- \rightarrow IO_3^- + 2I^- + 3H_2O \qquad \text{(Very Slow)}$$

Upon acidification, IO^-, HIO, IO_3^- are all converted to I_3^- so that the overall process is:

$$O_3 + 3I^- + H_2O \rightarrow I_3^- + O_2 + 2OH^-$$

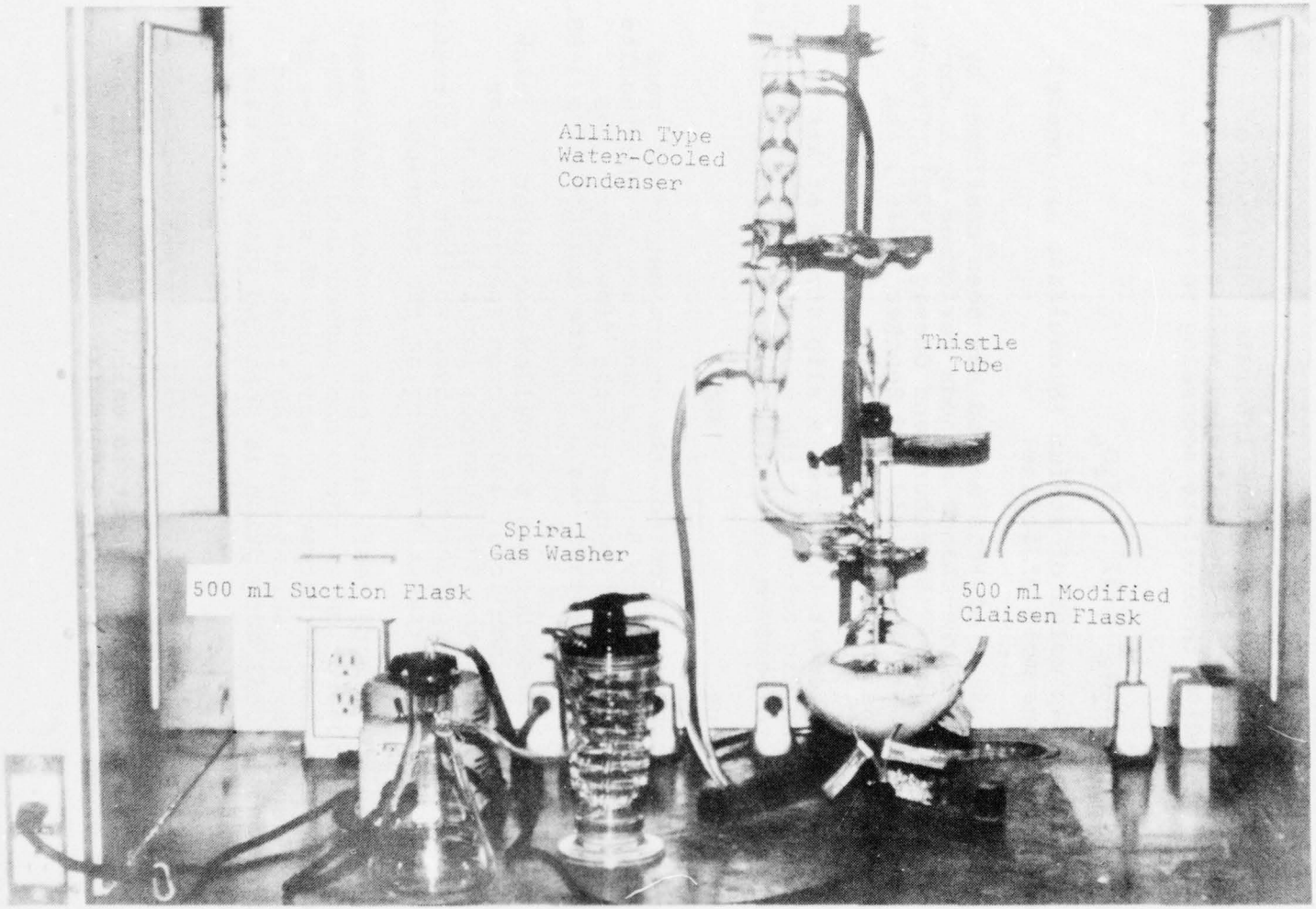

Figure A-1. Cyanide Distillation Apparatus

Thus, one mole of ozone liberates one mole of iodine. The iodine is then titrated with a standardized solution of sodium thiosulfate according to the following reaction:

$$I_3^- + 2S_2O_3^= \quad 3I^- + S_4O_6^=$$

Thus, two moles of sodium thiosulfate are needed to react with one mole of iodine.

The accuracy of this method has been confirmed by comparison with volume-change methods performed by a number of investigators: Ladenburg and Ouasig (1901), Treadwell and Anneler (1903), Reisenfeld and Bencker (1916), and Birdsell, Jenkins and Spadinger (1962).

In the present instance, a slip stream of air containing ozone was taken off the main stream (main output) in order to perform the titration on a reasonable scale.

b. Apparatus

The apparatus used for the determination of ozone output is shown in Figure A-2. The accuracy of the results is dependent on the preciseness of the flowmeter. The flowmeter used in this case was a Schutte and Koerting 3-RB.

The gas absorber was a 2-gallon container in which was submerged a 6-inch long, 100 micron sparger. After bubbling ozone into the gas absorber for a specified length of time, the sparger was removed so that the titration could be performed without transferring the solution.

For a 5-minute test, this gas absorber gives essentially total absorption of the ozone passed into it. The flow rate used ranged between 30 scfh and 85 scfh. Use of a second absorber in series with the first has confirmed that reliable total absorption is obtained with a single unit.

c. Calculations

The slip stream output is calculated in grams per hour of ozone by the following formula:

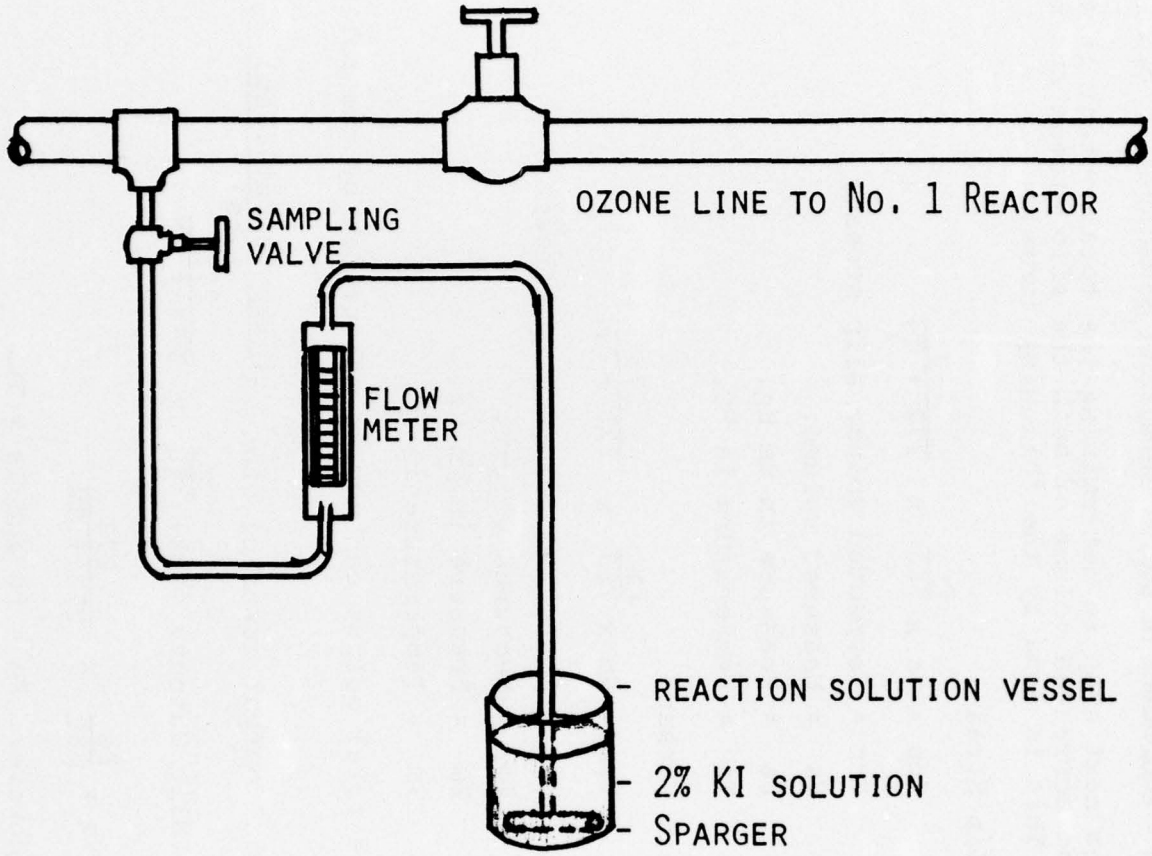

Figure A-2. Ozone Output Test Apparatus

$$\text{gm/hr of ozone} = \frac{(\text{Normality of } Na_2S_2O_3 \cdot 5H_2O)(\text{mls } Na_2S_2O_3 \cdot 5H_2O)\frac{60 \text{ min/hr}(48)}{5 \text{ min.}}}{2 \times 1{,}000 \text{ ml/l}}$$

Where: 48 = molecular weight of ozone.

2 = equivalent of sodium thiosulfate pentahydrate to ozone.

The next step in determining the total output is to calculate the corrected volume of both the slip stream and main stream. This is done by the following formula:

Slip Stream:

$$Vcs = Vs \times \frac{Ps}{760} \times \frac{273}{273 + Ts}$$

Where: Vcs = Corrected volume slip stream.

Vs = Measured volume.

Ps = Pressure in mm Hg.

Ts = Temperature in ^{o}C.

Main Stream:

$$Vcm = Vm \times \frac{Pm}{760} \times \frac{273}{273 + Tm}$$

Where: Vcm = Corrected volume main stream.

Vm = Measured volume.

Pm = Pressure in mm Hg.

Tm = Temperature in ^{o}C.

The total output can now be calculated by the following formula:

$$\text{Total output gm/hr of ozone} = \frac{(\text{Slip Output})(Vcm)}{(Vcs)}$$

$$= (\text{Slip Output})\,(Vmk)\,\frac{Pm}{760} \times \frac{273}{273 + Tm}$$

$$Vs \times \frac{Ps}{760} \times \frac{273}{273 + Ts}$$

However, Pm = Ps and Ts = Tm.

$$\therefore \text{Output (gm/hr)} = \frac{(\text{Slip Output})(Vm)}{(Vs)}$$

3. FILTRABLE SOLIDS

The filtrable solids were collected by drawing the waste sample through a millipore filter assembly connected to a vacuum. The filter membrane used in this assembly had a 0.47 micron pore size.

All filter membranes were pre-dried in an oven for 2 hours at 37°C, then cooled in a desiccator for 1 hour before weighing. A balance that gives weight to the nearest 0.1 mg was used.

The sample size for filtration ranged from 100 mls to 250 mls. Each filtration took approximately 10 minutes, including three washings with distilled water. The filter membranes (after filtration) were dried in an oven for 4 hours at 37°C, then cooled in a desiccator for 1 hour before weighing.

The weight of the solid was calculated by subtracting the membrane weight from the solid plus membrane weight. This value was then used in the following formula:

$$\text{mg/l of filtrable solid} = \frac{A \times 1000}{\text{sample size}}$$

Where A = weight of the filtrable solid expressed in milligrams.

4. pH MEASUREMENT

All pH measurements were performed electrometrically using method 144 from reference 6.

5. METALS ANALYSIS

All metal analyses were performed using a Perkin-Elmer atomic absorption spectrophotometer Model 360. The metal determinations were performed using the standard addition method (Reference 6) to correct for background interferences. The conditions for each metal analysis were then outlined in the manual supplied by Perkin-Elmer entitled, "Analytical Methods for Atomic Absorption Spectrophotometry."

ABBREVIATIONS AND SYMBOLS

CN (or CN^-)	Cyanide (ion)
CNO (or CNO^-)	Cyanate (ion)
EDTA	Ethylenediaminetetraacetic Acid
Fe	Iron
HCl	Hydrogen Chloride (Hydrochloric Acid)
HCN	Hydrogen Cyanide
H_2O	Water
I^-	Iodide ion
KI	Potassium Iodide
Na^+	Sodium ion
NaCl	Sodium Chloride
NaCN	Sodium Cyanide
NaCNO	Sodium Cyanate
NaOCl	Sodium Hypochlorite
NaOH	Sodium Hydroxide
Na_2SO_3	Sodium Sulfite
NH_3	Ammonia
$(NH_4)_2CO_3$	Ammonium Carbonate
Ni	Nickel
O_2	Oxygen
O_3	Ozone
OCl (or OCl^-)	Hypochlorite (ion)
OH^-	Hydroxide ion
Si	Silicon
$S_2O_3^=$	Thiosulfate ion

ABBREVIATIONS AND SYMBOLS (Concluded)

AFB	Air Force Base
BTU	Energy, British Thermal Units
^{o}C	Temperature, Degrees Centrigrade
cfh, CFH	Flow Rate, Cubic Feet per Hour
cfm, CFM	Flow Rate, Cubic Feet per Minute
dia.	Diameter
^{o}F	Temperature, Degrees Fahrenheit
g/hr	Flow Rate, Grams per Hour
gal	Volume, Gallon
gph	Flow Rate, Gallons per Hour
gpm	Flow Rate, Gallons per Minute
hp	Horsepower
kw	Power, Kilowatts
kwh	Energy, Kilowatt-Hours
l	Volume, Liter
lb/hr	Flow Rate, Pounds per Hour
mg/l	Concentration, Milligrams per Liter
ml	Volume, Milliliter
ml/min	Flow Rate, Milliliters per Minute
pH	Measure of Acidity
ppm	Concentration, Parts per Million
psig	Pressure, Pounds per Square Inch, Gauge
scfm, SCFM	Flow Rate, Standard Cubic Feet per Minute
UV	Ultraviolet Light or Energy

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INITIAL DISTRIBUTION

Hq USAF/PREE	1	ASD/DEP	1
Hq USAF/RDPS	2	ASD/SMKF	1
Hq USAF/SAFOI	1	RADC/DOT	1
Hq USAF/SGPA	2	AEDC/DEE	1
Hq USAF/PREVP	1	SAMTEC/SEH	1
Hq COMD USAF/DEE	1	AMD/RDU	1
ADC/DEEV	2	ADTC/CSV	1
CINCAD/SGPAP	1	ADTC/DLOSL (Tech Library)	1
AFCS/DEEE	1	AFFTC/DE	1
AFLC/SGB	1	AFCEC/XR (Tech Library)	12
AFLC/DEPV	1	AFCEC/EV	12
AFLC/MAUT	1	AFETR/DER	1
AFLC/MMRF	1	ESD/DE	1
AFSC/DE	1	USAF Rgn Civ Engr	3
AFSC/SD	1	SAMMA/MAGCB	1
AFSC/DEV	1	USAFSO/DEE	1
AFSC/SGB	1	DDC/TCA	12
AFSC/SGPE	1	AFPA	1
ATC/DEPV	1	Defense Rsch & Engr/AD (E&LS)	1
ATC/SGPAP	1	OASD/Health & Environ	2
AAC/DEV	1	Ch of Engr/ENGMC-RD	1
AAC/SGB	1	Dir, USA WW Exp Stn	1
MAC/SGPE	1	USA CERL	1
MAC/DEEE	1	Dir, USA Eng R&D Lab/MERDC	1
CINCPACAF/DEMU	2	Ch of R&D/Dept of the Army	
CINCPACAF/SGPE	1	DAED-ARE-E	1
CINCSAC/DEPV	1	Chief of Naval Ops/Environ	
CINCSAC/SGPA	1	Protection Div, OP-45	1
TAC/DEEV	1	Naval Air Dev Ctr/MAE	1
TAC/SGPB	1	Naval Ship R&D Ctr/Code 3021	1
USAFSS/DEMM	1	Technology Transfer Staff (EPA)	1
CINCUSAFE/Surgeon	1	Office of Research & Dev	1
CINCUSAFE/DEPV	2	National Science Foundation	1
AFRES/DEEE	1	US Army Med Bioengr R&D Lab	1
USAFA/DEV	1		
AFIT/DEM	1		
AU/LDG	1		
AUL (AUL/LSE-70-239)	1		
AU/Surgeon	1		
AFOSR	1		
AFML/DO (Library)	1		
USAF Environmental Health Lab	2		
AFWL/SUL (Tech Library)	1		
USAFSAM/EDE	2		
AFRPL/Library	1		
FTD/LGM	1		
ASD/ENFPA	1		

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